This is a digital copy of a book that was preserved for generations on library shelves before it was carefully scanned by Google as part of a project to make the world's books discoverable online.

It has survived long enough for the copyright to expire and the book to enter the public domain. A public domain book is one that was never subject to copyright or whose legal copyright term has expired. Whether a book is in the public domain may vary country to country. Public domain books are our gateways to the past, representing a wealth of history, culture and knowledge that's often difficult to discover.

Marks, notations and other marginalia present in the original volume will appear in this file - a reminder of this book's long journey from the publisher to a library and finally to you.

Usage guidelines

Google is proud to partner with libraries to digitize public domain materials and make them widely accessible. Public domain books belong to the public and we are merely their custodians. Nevertheless, this work is expensive, so in order to keep providing this resource, we have taken steps to prevent abuse by commercial parties, including placing technical restrictions on automated querying.

We also ask that you:

+ *Make non-commercial use of the files* We designed Google Book Search for use by individuals, and we request that you use these files for personal, non-commercial purposes.

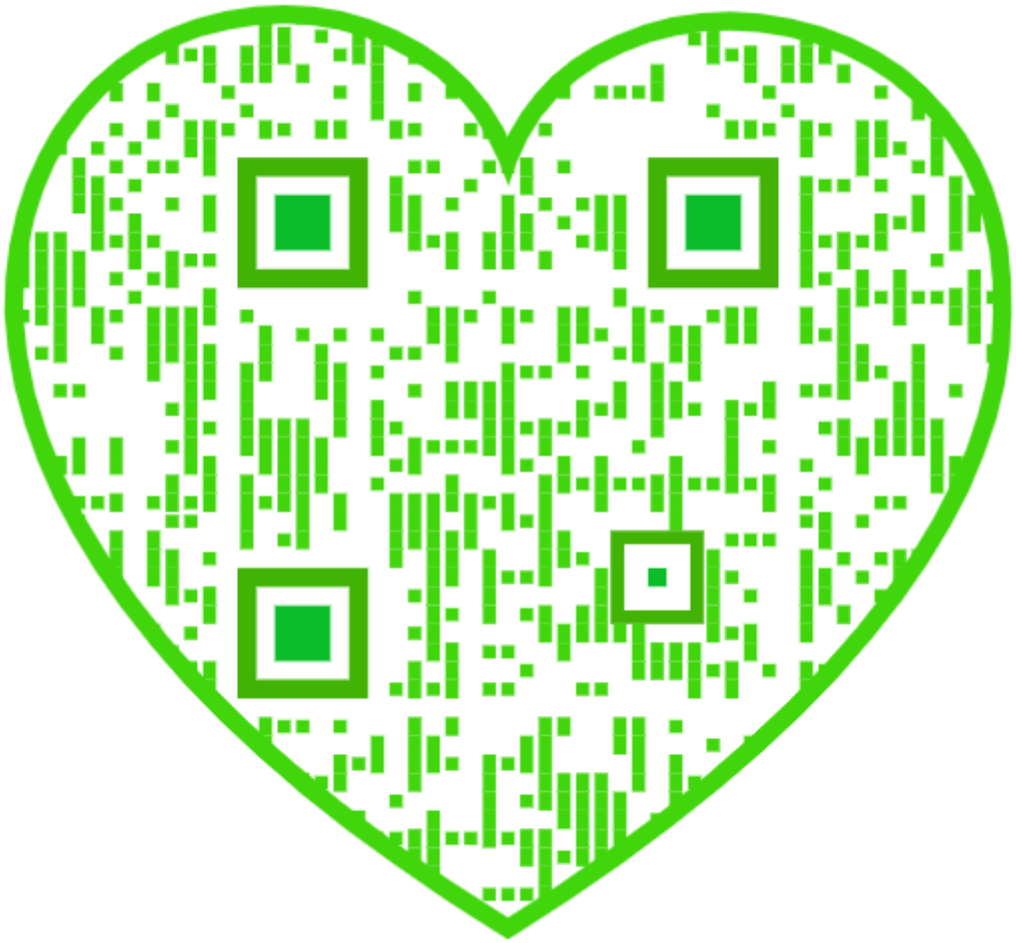
+ *Refrain from automated querying* Do not send automated queries of any sort to Google's system: If you are conducting research on machine translation, optical character recognition or other areas where access to a large amount of text is helpful, please contact us. We encourage the use of public domain materials for these purposes and may be able to help.

+ *Maintain attribution* The Google "watermark" you see on each file is essential for informing people about this project and helping them find additional materials through Google Book Search. Please do not remove it.

+ *Keep it legal* Whatever your use, remember that you are responsible for ensuring that what you are doing is legal. Do not assume that just because we believe a book is in the public domain for users in the United States, that the work is also in the public domain for users in other countries. Whether a book is still in copyright varies from country to country, and we can't offer guidance on whether any specific use of any specific book is allowed. Please do not assume that a book's appearance in Google Book Search means it can be used in any manner anywhere in the world. Copyright infringement liability can be quite severe.

About Google Book Search

Google's mission is to organize the world's information and to make it universally accessible and useful. Google Book Search helps readers discover the world's books while helping authors and publishers reach new audiences. You can search through the full text of this book on the web at `http://books.google.com/`



Journal

American Leather Chemists Association

Digitized by Google

FORESTRY
LIBRARY

Digitized by Google

Digitized by Google

Digitized by Google

The Journal of the

American Leather Chemists

Association

VOLUME VII, 1912

PUBLISHED MONTHLY BY
THE AMERICAN LEATHER CHEMISTS
ASSOCIATION

THE CHEMICAL PUBLISHING CO., PRINTERS
EASTON, PA.

Digitized by Google

TS940
A6
v.7
FORESTRY
LIBRARY

UNIV. OF
CALIFORNIA

Digitized by Google

The Journal of the

American Leather Chemists Association

INDEX TO VOLUME VII, 1912

In this index (P) indicates a patent, and (A) an abstract.

INDEX OF AUTHORS' NAMES

ABT, G., Origin of Salt Stains 492
ADAMS, S. H., Treating Sewage, (P) 343
AITKEN, W., Extracts, (A) 582
ALSOP, E. C., Purification of Liquid Tannery Waste 72
ALSOP, W. K., Comparative Extract Analysis 527
ANDREIS, E., The Process of Liming 609
APPELIUS, W., Purification of Water Waste from Tanneries, (A) 342
APPELIUS, W., Valuation of Cold Soluble Quebracho Extract, (A) 130
ARMSTRONG, P. M. C., Device for Pipetting Dangerous Liquids 398
AULSON, J. W., Hide-Working Machine, (P) 50

BALDERSTON, L., Acidity of Tan Liquors 665
BALDERSTON, L., Device for Pipetting Dangerous Liquids 262
BALDRACCO, G., Analysis of Fats, (A) 125
BECKER, H., Process of Puering Hides and Skins, (P) 234
BENNETT, H. G., Analytical Examination of Bating, (A) 173
BENNETT, H. G., Acidity of Tanning Liquors, (A) 382, 571
BESSON, A. A., The Salting of Hides, (A) 578
BESSON, A. A., Lactic Acid Analysis, (A) 48
BIDDLE, H. C., AND KELLEY, W. P., Tannic Acid, Ethyl Gallate and the supposed Ester of Tannic Acid 433
BLOCKLEY, J. R., AND MEHD, P. V., Estimation of Sulphides in Lime Liquors 358
BLOCKLEY, J. R., AND PARKER, J. G., Value of Non-tans in Tanning Materials and Extracts 192
BLOCKLEY, J. R., The Soaking of Dried Hides by means of Formic Acid 467
BLOXAM, A. G., Leather Embossing Machine, (P) 584
BOEHRINGER, C. H., Process of Deliming Hides and Skins, (P) 393
BRUSH, W. D., AND MELL, C. D., Quebracho Wood and its Substitutes 481

CAMBON, V., Manufacture of Oils from Fish Refuse, (A) 123
CARTER, J. G., Red Mangrove Bark in Madagascar, (A) 175
CHAMBARD, P. E., Preparation of Hides for Tannage, (P) 131
CHAPLET, A., The Dyeing of Leathers, (A) 575
CHERCHEFFSKY, N., AND ESCUDIE, R., Origin of Some Lubricating Oils, (A) 233
CHERCHEFFSKY, W. N., Determination of Mineral Oil in Olein, (A) 278
CLAFLIN, A. A., Chrome Tannage Costs, (A) 444
CLAFLIN, A. A., Popular Illusions in Regard to Tanning, (A) 632
CLAFLIN, A. A., Tanning Properties of Waste Sulphite Cellulose Liquors 154
CLAFLIN, A. A., White Pigments for Leather 274
CLAPP, A. L., Production of Stock for Leather-board, (P) 583
COOMBS, F. A., AND RUSSELL, G. H., Mangrove Bark of North Queensland and Manufacture of Mangrove Cutch, (A) 273
CORNE, C., Evaporating Apparatus, (P) 132

342814

Digitized by Google

DAS, B. M. AND STIASNY, E., A Contribution to the Chemistry of Chrome Tannage . 506
DAVIS, W. A., Estimation of Potassium 430
DRAKE, H. L., Bark-removing machine, (P) 234
DUNN, J. E., Evaporator, (P) 583

EACHUS, C., Methods for Oil Analysis 452
EBERLE, G., AND KRALL, L., Refuse from Puering Lamb Pelts, (A) 129
EITNER, W., Tannage for Weight, (A) 44
EITNER, W., Suede Leather from Foreign Hides, (A) 178
EITNER, W., Dyeing and Curring of Suede Leather, (A) 178
EITNER, W., Use of Antichlor in Vegetable Tannage, (A) 179
EITNER, W., Substitutes for Expensive Fats, (A) 179
EITNER, W., Governing Elements in Tannage of Kips, (A) 179
EITNER, W., Reactions of Tannins, (A) 230
EITNER, W., Swelling in Sole Leather Tannage, (A) 281
EITNER, W., Several New Fat Preparations for the Leather Industry, (A) 637
EITNER, W., Hide Preservation and Glue Leather, (A). 641
EKSTROM, P. G., Method of Producing Alcohol from Sulphite-Cellulose Lyes, (P) . . 583
ELSON, G. D., AND LIVERSEEGE, J. S., Tests for Linseed Oil and its Adulterants, (A) . 275
ESCUDIE, R., AND CHERCHEFFSKY, N., Origin of Some Lubricating Oils, (A) 233

FAHRION, W., Chemistry and Analysis of Fats for 1911, (A) 503
FAHRION, W., Neats-foot Oil, (A) 223
FARRAR, W., AND YOUNG, S., Boarding Machine, (P) 182
FEIST, K., AND HAUN, H., Tannin in Chinese Gall Nuts, (A) 691
FISCHER, E., AND FREUDENBERG, K., Tannin and the Sythesis of Similar Substances, (A) 390
FORSTER, J., Process and Materials for Treating Hides and Skins, (P) 504
FORSTER, J., Tannage, (P) 394
FREUDENBERG, K., (See Fischer, E.).
FRIEDENBERGER, O., Manufacturer of Lactic Acid, (P) 393
FRIEDLANDER, D., Hide-Working Machine, (P) 49
FROST, P. F., Waterproofing Compound for Leather, (P) 182

GANSSER, A., Detection of Sulphide-Cellulose Extract in Leather, (A) 635
GANSSER, A., Testing of Extracts with Animalized Cotton, (A) 642
GARELLI, F., Tannage by Means of Salts of Cerium, (A) 575
GAY, J. H., Leather-Splitting Machine, (P) 694
GLASEL, C. J., Hide-Treating Machine, (P) 583
GOODRICH, C. E., AND WALTER, H. L., Fat Extraction Apparatus, (P) 50
GRASSER, G., Use of Chrome Leather in the Valuation of Tanning Extracts, (A) . . . 225
GRASSER, G., Determination of Acids in Tan Liquors, (A) 278
GRASSER, G., Employment of Coal Tar Dyes for Leather and Furs, (A) 340
GRASSER, G., Chemical Investigation of Substances in Birch, (A) 42
GRIMM, M., Lactic Acid Fermentation, (A) 277
GROSSERON, T., (See Rappin). 573
GROSSMAN, J., Sewage Sludge and its Disposal, (A) 176
GIUSIANA, E. A., New Process of Liming, (A) 682
GIUSIANA, E. A., Decolorization of Tanning Extracts, (A) 682
GURNEY, H. P., Method of Measuring Absolute Viscosity, (A) 227

HAAS, C., Tanning-drum, (P) 584
HALL, W. G., AND SEARBY, W., Evaporator, (P) 583
HARRISON, L. H., Permutit System of Water Treatment 423
HAUN, H., AND FEIST, K., Tannin in Chinese Gall Nuts, (A) 691
HEALY, H. W., Are Tanners Teaching Their Superintendents How to Think? 31
HEAVEN, G. S., AND WILSON, L. P., New Oxygen Absorption Method for Oils, (A) . . 445
HENDERSON, A. H., Composition of Matter, (P) 283
HENDERSON, A. H., Treatment of Rawhide, (P) 283
HENDERSON, A. H., Fabric or Cloth, (P) 284
HILDEBRAND, J., Comparative Valuation of Deliming Agents, (A) 446

Digitized by Google

HILL, F. D., European Wool and Leather Grease, (A) 226
HOPPENSTEDT, A. W., Seal Oil 13
HOPPENSTEDT, A. W., The Tannins 87, 170
HOPPENSTEDT, A. W., Detection of Tanning Materials 664
HOUGH, A. T., Swelling and Solubility of Hide by Acids, (A) 385
HUBER, VON, AND MARCUSSON, Testing for Fish Oil, (A) 181

ILJIN, L. F., Composition of Tannin, (A) 131

JAMES, F. P., Process of Curing Hides, (P) 343
JETTMAR, J., Neutralization of Chrome Leather, (A) 639
JOUVE, A., Salt Stains, (A) 573
JOYA, R., Apparatus for Evaporating, (P) 182

KAYSER, H., Evaporating Apparatus, (P) 584
KELLEY, W. P., (See Biddle, H. C.).
KESTNER, P., Evaporating Apparatus, (P) 182, 394
KERR, G. A., AND WILSON, W. F., Acids in Chestnut Wood and Tannery Liquors . . 77
KNOWLES, G. E., Use of Tannin Materials and Their Analysis, (A) 391
KOHNSTEIN, B., Chrome Tannage, (A) 124
KOHNSTEIN, B., Report of Research Institute for Leather Industry, (A) 125
KOHNSTEIN, B., Coefficient of Expansion of Oils, (A) 233
KOHNSTEIN, B., Tests for Vegetable Tanning Materials, (A) 449
KOHNSTEIN, B., The Theory of Tannage, (A) 575
KOHNSTEIN, B., Decolorization and Clarification of Tanning Extracts, (A) 575
KORNACHER, F., Process of Making Non-Slipping Leather, (P) 584
KRALL, L., AND EBERLE, G., Refuse from Puering of Lamb Pelts, (A) 129
KREISMANN, P., AND VOEDISH, H. A., Chrome Compound from Leather Scraps, (P) . 584
KUDLACEK, E., AND WLADIKA, J., Action of Sulphuric Acid in Extraction, (A) . . . 642

LAW, D. J., I. A. L. T. C. Conference, 1912 586
LAW, D. J., (See Wood. J. T.).
LEWKOWITSCH, J., AND WOOD, J. T., Oil Tannage, (P) 694
LIPMAN, J. F., Artificial Leather, (P) 694
LINDSTROM, J. H., Process of Tanning, (P) 694
LIVERSEEGE, J. S., AND ELSON, G. D., Tests for Linseed Oil and Its Adulterants, (A) . 275
LOCKWOOD, A. H., Development of Leather Industry and Its Relation to World's Hide Supply 35
LOUGEE, C. A., Cylinder for Leather-shaving Machines, (P) 182
LOVELAND, F. M., Analysis of Sulphite-Cellulose Extracts 368
LOVELAND, F. A., Tannery Sewage Disposal 474

MACGREGOR, J., Evaporator, (P) 583
MCNEIL, H. C., Calcium Carbide Method for Determination Moisture, (A) 630
MANNING, R. G., AND NIERENSTEIN, M., Constitution of Tannin, (A) 502, 582
MANSTETTEN, L., Vegetable Tanning Liquors, (A) 688
MARCUSSON, AND HUBER, VON, Testing for Fish Oils, (A) 181
MEHD. P. V., AND BLOCKLEY, J. R., Estimation of Sulphides in Lime Liquors 358
MELL, C. D., AND BRUSH, W. D., Quebracho Wood and Its Substitutes 481
MERRILL, H. C., Colors and Their Application to Leather 15
MEUNIER, L., AND SEYEWETZ, A., Tanning of Gelatine and Hide, (A) 222
MEUNIER, L., AND SEYEWETZ, A., Formation of Leather by Dehydration, (A) 230
MEUNIER, L., Formaldehyde Tannage, (A) 574
MEUNIER, L., Purification of Tannery Effluents, (A) 687
MIELCK, H., Use of Zoul's Method for Titration of Fats, (A) 232
MILLER, J. S., Sewage Separator, (P) 283
MOELLER, W., Effect of Difficult Soluble Ingredients of Quebracho Extract upon Rendement, (A) 43
MULLER, P., Evaporator, (P) 583

Digitized by Google

NEWHALL, G. M., Separator for Vacuum Pans, (P) 182
NEUMANN, R., A Simplification in the Estimation of Nitrogen, (A) 636
NIERENSTEIN, M., Constitution of Tannin, (A) 279, 579
NIERENSTEIN, M., AND MANNING, R. J., Constitution of Tannin, (A) 502, 582

OBERFELL, C. R., The Composition of Leather from Different Parts of the Hide . . . 27
OBERFELL, C. R., Report of Oils and Fats 656
O'KEEFE, D., Composition for Treatment of Leather, Fabrics, etc., (P) 284
OSBORNE, H. M., Drying of Hides and Soaking of Dried Hides, (A) 228
ORDWAY, C., Vacuum Evaporating Apparatus, (P) 49
OTTO, M. P., Purification of Water and Sewage by Ozone, (P) 393

PAESSLER, DR. J., Result of Researches on Mangrove Barks, (A) 46
PAESSLER, J., Report of Freiberg Experiment Station for 1911 (A) 231
PAESSLER, J., The Salting of Hides and Skins, (A) 392
PAESSLER, J., Exact Methods for Taking Samples, (A) 445
PAESSLER, J., Report of Analysis Commission of the German Section, (A) 577
PAESSLER, J., Fat Content of Belting Leather, (A) 638
PANIKER, M. A. R. AND STIASNY, E., Acid Character of Gallotanic Acid, (A) 263
PARKER, J. G., AND BLOCKLEY, J. R., Value of Non-tans in Tanning Materials and Extracts 192
PARKER, J. G., Valonia 400
PAYNE, E. E. M., Production of Leather, (P) 694
PIRLOT, A., Tanning Materials of Belgian Congo. (A) 681
POLLAK, L., Tanning Materials and Extracts, (A) 279
POLLAK, L., Kohnstein's New Identification of Tannin, (A) 449
POWARNIN, G., Practical Questions from the Chemistry of the Tanstuffs, (A) 337
POWER, J. A., Evaporating Apparatus, (P) 394
PROCTER, C. M., Myrobalans, (A) 632
PROCTER, H. R., The Mutual Relations of the A. L. C. A., and the I. A. L. T. C. 10
PROCTER, H. R., Acids in Tan Liquors 249
PROCTER, H. R., Are You Keeping Pace with Chemistry? 607

QUIRIN, E. J. F., Leather-staking Machine, (P) 584

RAPPIN, T. GROSSERON, AND SOUBRANNE, L., Causes of Salt Stains and Means of Avoiding Them, (A) 573
RANDALL, G., Tanners' Problems, (A) 583
REED, H. C., Value of Non-tans in Extracts 204
REED, H. C., Analysis of Vegetable Tanning Materials 307
REDLICH, A., Process for Clarifying Tanning Liquors, (P) 234
REIDEL, E., Artificial Leather, (P) 694
RICHARDSON, F. W., AND WALTON, W. K., Turkey Red Oil, (A) 229
ROENITZ, L. T., Lime and its Preparation 165
ROGERS, J. S., AND VEITCH, F. P., Leather Analysis, A. L. C. A., 1912 645
RUSIECKI, W., Evaporating Machine, (P) 284
RUSSELL, C. H., AND COOMBS, F. A., Mangrove Bark of North Queensland and Manufacture of Mangrove Cutch, (A) 273

SADLOW, CARL, Glue from Chrome Leather, (P) 49
SALOMON, T., Butyric Acid in the Tannery, (A) 501
SALOMON, M. S., AND SEABER, W. M., Importance of Chemical Control in the Leather Industries, (A) 569
SAND, H. J. S., (see WOOD, J. T.)
SANDBORN, T. F., Evaporating Apparatus, (P) 394
SARGARIAN, J., AND STEINKOPF, W., Composition of Tannin, (A) 131
SCHELL, E., Analysis of Tanning Extracts 209
SCHNEEMAN, G., Leather Fats and Oils, (A) 129
SCHNEIDER, J., Leather and Fur which will Resist Treatment with Boiling Water, (A) . 225
SCOTT, J., The Fungi of Excreta, (A) 177
SEABER, W. M., (See SALOMON, M. S.)
SEARBY, W., AND HALL, W. G., Evaporator, (P) 583
SELTZER, J. M., Use of Oil of Mustard as an Antiseptic 458

Digitized by Google

SEYEWETZ, A., (See Meunier, L.)
SEYMOUR-JONES, A., Restoration of Dry Hides and Skins, (A) . . . 336
SICHLING, H., Methods of Preparing Artificial Leathers, (A) . . . 575
SIEGFELD, DR. M., Estimation of Reichert-Meissl Value, (A) . . . 45
SIMACEK, V., Leather and Fur Which Will Resist Treatment with Boiling Water, (A) 225
SIMEON, E., Machine for Stretching Hides and Skins, (P) . . . 284
SIMON, E., Glove Leather, (P) . . . 284
SIMPSON, T. D., Methods for Testing Lubricating Oils . . . 235
SMITH, W. R., Machine for Brushing and Cleaning Leather, (P) . . . 284
SMITH, W. R., Method of Treating Leather, (P) . . . 343
SNODGRASS, J. H., Russian Tanning Industry, (A) . . . 635
SODY, L., Extracts of Cellulose . . . 373
SOUBRANNE, L., (See Rappin).
SPRAGUE, F. O., Free Sulphuric Acid in Tannery Liquors . . . 670
STAYNES, W. H., Buffing Roll, (P) . . . 504
STEINKOPF, W., AND SARGARIAN, J., Composition of Tannin, (A) . . . 131
STERN, L., Process of Unhairing Hides and Skins, (P) . . . 283
STERN-SONNEBORN, O., Oil-Testing Machine, (P) . . . 504
STIASNY, E., AND PANIKER, M. A. R., Acid Character of Gallotannic Acid, (A) . . . 263
STIASNY, E., Applied Chemistry in the Service of Tanning, (A) . . . 341
STIASNY, E., AND WILKINSON, C. D., Free H_2SO_4 in Leather . . . 461
STIASNY, E., Application of Law of Mass-Action . . . 301
STIASNY, E., Qualitative Detection and Differentiation of Vegetable Tannins. . . . 548
STIASNY, E., AND DAS, B. M., A Contribution to the Chemistry of Chrome Tannage . 506
STOCKBERGER, W. W., Tannin Plants of Paraguay . . . 185
STOCKTON, G. B., Tanning and Dressing Pigskins for Saddles, (A) . . . 176
STOCKTON, G. B., Manufacture of Belting Butts . . . 413
STRICKLER, E. H., Process of Making Anhydrous Sulphites and Bisulphites, (P) . . . 284
SWINTON, R. S., Manufacture of Volatile Organic Acids, (P) . . . 284

THOMPSON, W. P., Staking Machine, (P) . . . 182
THOMPSON, W. P., Leather Board, (P) . . . 343
THUAU, U. J., Analysis of Sulphonated Oils, (A) . . . 498
THUAU, U. J., Report of International Commission on Leather Analysis . . . 602
TRILLAT, A., Lactic Acid Bacillus, (A) . . . 276
TURNER, W. B., Leather-Glazing Machine, (P) . . . 504

VEITCH, F. P., AND ROGERS, J. S., Leather Analysis, A. L. C. A., 1912 . . . 645
VOEDISH, H. A., AND KREISMANN, P., Chrome Compound from Leather Scraps, (P) . 584

WADDINGTON, J. S., Treatment of Sewage, (P) . . . 283
WALTER, H. L., AND GOODRICH, C. E., Fat Extraction Apparatus, (P) . . . 50
WALTON, W. K., AND RICHARDSON, F. W., Turkey Red Oil, (A) . . . 229
WATRIGANT, H. L., Process for Recovering Nitrogen, (P) . . . 583
WILKINSON, C. D., AND STIASNY, E., Free H_2SO_4 in Leather . . . 461
WILLIAMSON, G., Impregnating Leather with Solid Lubricants, (P) . . . 584
WILSON, W. F., AND KERR, G. A., Acids in Chestnut Wood and Tannery Liquors . . . 77
WILSON, L. P., AND HEAVEN, G. S., New Absorption Method for Oils, (A) . . . 445
WISDOM, R. H., What is Tannin? . . . 371
WISDOM, R. H., Notes on Color Valuation of Tanning Materials . . . 395
WITHEY, R., Rubberizing Hides, (P) . . . 182
WLADIKA, G., AND KUDLACEK, E., Action of Sulphuric Acid in Extraction, (A) . . . 642
WOLFF, A., Preparation of Chrome Leather, (P) . . . 284
WOOD, J. T., SAND, H. J. S., AND LAW, D. J., Method for Quantitative Determinations of the Falling of Skin in the Puering or Bating Process . . . 253
WOOD, J. T., AND LAW, D. J., Preliminary Report on Light Leather Liming Control . 346
WOOD, J. T., Rising or Pickling of Skins . . . 409
WOOD, J. T., AND LEWKOWITSCH, J., Oil Tannage, (P) . . . 694
YOCUM, J. H., Characteristics and Commercial Adaptability of Hides . . . 135
YOUNG, S., AND FARRAR, W., Boarding Machine, (P) . . . 182

Digitized by Google

INDEX OF SUBJECTS

Acids, Manufacture of Volatile Organic, R. S. Swinton, (P) 284
in Chestnut Wood and Tannery Liquors, G. A. Kerr and W. F. Wilson, ... 77
in Tan Liquors, H. R. Procter, ... 249
, Determination of —, G. Grasser, (A) 278
, Hugh Garner Bennett, (A) 382, 571
A. L. C. A., Mutual Relation of the—and the I. A. L. T. C., H. R. Procter 10
Alcohol, Method of Producing—from Sulphite-cellulose Lyes, P. G. Eckstrom, (P) . . 583
Analysis Commission of the German Section, Report of the—, J. Paessler, (A) 577
, Comparative Extract—, W. K. Alsop 527
of Vegetable Materials Containing Tannin, Proposed Official Method of the A. L. C. A. for the—, ... 294
Antichlor in Vegetable Tannage, Use of—, W. Eitner, (A) 179
Bacillus, Lactic Acid—, A. Trillat, (A) 276
Bark, Machine for Removing—, from Logs, F. Libert (P) 182
Bark-removing Machine, H. L. Drake, (P) 234
Bating, Analytical Examination of—, H. G. Bennett, (A) 173
Belgian Hide Trade Methods, (A) 390
Belting Butts, Manufacture of—, G. B. Stockton 413
Birch, Chemical Investigation of Substances in—, G. Grasser, (A) 42
Bisulphites, Process of Making Anhydrous Sulphites and—, E. H. Strickler, (P) . . . 284
Bleaching of Upper Leather, (A) 448
Boarding Machine, W. Farrar and S. Young, (P) 182
Buffalo Robes, (A) 633
Buffing Roll, W. H. Staynes, (P) 504
Butyric Acid, (A) 389
in the Tannery, T. Salomon, (A) 501
Calf Skins, Dyeing—, (A) 692
Cellulose, Extracts of—, L. Sody 373
Changes in Methods, Report of Proposed—, ... 2
Chamois Leather, (A) 277
Chemistry, Are You Keeping Pace With—? H. R. Procter 607
Chrome Box-calf, Preparation of—, (A) 44
Compounds from Leather Scraps, H. A. Voedish and P. Kreismann, (P) . . . 584
Leather, The French Government, and —, ... 627
Neutralization of—, J. Jettmar, (A) 639
Preparation of—, A. Wolff, (P) 284
Use of—, in the Valuation of Tanning Extracts, G. Grasser, (A) . . 225
Sole Leather, ... 625
Tannage, B. Kohnstein, (A) 124
, A Contribution to the Chemistry of—, E. Stiasny and B. M. Das . . 506
Costs, A. A. Claflin, (A) 444
Coal Tar Dyes, Employment of—, for Leather and Furs, G. Grasser, (A) 340
Colors and Their Application to Leather, H. C. Merrill 15
Color Valuation of Tanning Materials, Notes on—, R. H. Wisdom 395
Degreasing Materials, New—, W. Eitner, (A) 335
Deliming Agents, Comparative Valuation of—, J. Hildebrand, (A) 446
Drenching, Lactic Acid for—, (A) 683
Drying Hides, Process of—, W. H. Allen, (P) 49
Effluents, Purification of Tannery— 243
Electric Heater for Ether Extraction, (A) 122
Emory Oak, (A) 573
Ethyl Gallate and the Supposed Ester of Tannic Acid, H. C. Biddle and W. P. Kelley 433
Evaporating Apparatus, C. Corne, (P) 132
, R. Goya, (P) 182
, P. Kestner, (P) 182, 394
, Vacuum—, C. Ordway, (P) 49
, W. Rusiecki, (P) 284

Digitized by Google

Evaporating Apparatus, J. A. Powers, (P) . . . 394
, T. F. Sandborn, (P) . . . 394
, H. Kayser, (P) . . . 584
Evaporator, J. MacGregor, (P) . . . 583
, G. E. Dunn, (P) . . . 583
, P. Muller, (P) . . . 583
, W. G. Hall, and W. Searby, (P) . . . 583
Excreta, The Fungi of—, J. Scott, (A) . . . 177
Extraction, The Action of Sulphuric Acid in—, J. Wladika and E. Kudlacek, (A) . . 642
Extract Analysis, Notes on—, . . . 397
Extracts, W. Aitken, (A) . . . 582

Fat Extraction Apparatus, H. L. Walter and C. E. Goodrich, (P) . . . 50
Fats, Analysis of—, Dr. Baldracco, (A) . . . 125
, Chemistry and Analysis of—, for 1911, W. Fahrion, (A) . . . 503
, Substitutes for Expensive—, W. Eitner, (A) . . . 179
, Use of Zoul's Method for Titration of—, H. Mielck, (A) . . . 232
Fat Preparations, Several New—, for the Leather Industry, W. Eitner, (A) . . . 637
Fermentation, Lactic Acid—, M. Grimm, (A) . . . 277
Fish Oils, Testing for—, Marcusson and von Huber, (A) . . . 181
Fleshing Machines for Heavy Hides, Use of—, (A) . . . 124
Freiberg Experiment Station, Report of—, for 1911, J. Paessler, (A) . . . 231
Gallotannic Acid, Acid Character of—, M. A. R. Paniker and E. Stiasny, (A) . . . 263
Glue from Chrome Leather, Carl Sadlow, (P) . . . 49
Goatskins, How to Tan—, (A) . . . 685
Grease, European Wool and Leather—, (A) . . . 226
Hemlock, Western, (A) . . . 632
Hide, Composition of Leather from Different Parts of the—, C. R. Oberfell . . . 27
Supply, World's—, A. H. Lockwood . . . 35
-working Machine, D. Friedlander, (P) . . . 49
, J. W. Aulson, (P) . . . 50
, Swelling and Solubility of—, by Acids, A. T. Hough, (A) . . . 385
-treating Machine, C. J. Glasel, (P) . . . 583
Preservation, W. Eitner, (A) . . . 641
Hides for Tannage, Preparation of—, P. E. Chambard, (P) . . . 131
, Rubberizing—, R. Withey, (P) . . . 182
, Drying of—, and Soaking of Dried—, H. M. Osborne, (A) . . . 228
and Skins, Machine for Stretching—, E. Simeon, (P) . . . 284
, Restoration of Dry—, A. Seymour-Jones, (A) . . . 336
, Process of Curing—, F. P. James, (P) . . . 343
and Skins, The Salting of—, J. Paessler, (A) . . . 392
, Process of Deliming, H. Boehringer, (P) . . . 393
, Report on Preservation, Cure and Disinfection of—. . . . 487
, Process and Materials for Treating—, J. Forster, (P) . . . 504
, Characteristics and Commercial Adaptability of—, J. H. Yocum . . . 135
, The Soaking of Dried—, by means of Formic Acid, J. R. Blockley . . . 467
, Tanning—, with the Hair on, (A) . . . 576
, The Salting of—, A. Besson, (A) . . . 578

I. A. L. T. C., Conference, 1912, D. J. Law . . . 586
, Conference of—, . . . 451
, Meeting of German Section, (A) . . . 497
, Mutual Relations of the A. L. C. A. and the—, H. R. Procter . . . 10
Kips, Governing Elements in the Tannage of—, W. Eitner . . . 179

Lace Leather, Manufacture of—, (A) . . . 122
Lactic Acid Analysis, A. A. Besson, (A) . . . 48
For Drenching, (A) . . . 683
, Manufacture of—, O. Friendenberger, (P) . . . 393
Law of Mass—Action, Application of—, E. Stiasny . . . 301
Leather Analysis, A. L. C. A., 1912, F. P. Veitch and J. S. Rogers . . . 645
Analysis, Report of International Commission on—, U. J. Thuau . . . 602

Digitized by Google

Leather Analysis, Discussion of Report on—, ... 91
, Artificial—, J. F. Lipman, (P) 694
, Artificial—, E. Reidel, (P) 694
Belting, Fat Content of—, J. Paessler, (A) 638
, Board, W. P. Thompson, (P) 343
, Composition of—, from Different Parts of the Hide, C. R. Oberfell 27
, Chrome Sole—, ... 625
' Drum Tanned—, (A) 633
, Dyeing of—, A. Chaplet, (A) 575
Embossing Machine, A. G. Bloxam, (P) 584
, Fabrics, Etc., Composition for the Treatment of—, D. O'Keeff, (P) 284
, Formation of—, by Dehydration, L. Meunier and A. Seyewetz, (A) 230
For Bookbinding, (A) 687
, and Fur which will Resist Treatment with Boiling Water, J. Schneider and V. Simacek, (A) 225
—Glazing Machine, W. B. Turner, (P) 504
, Glove—, E. Simon, (P) 284
, Glue—, W. Eitner, (A) 641
, Goatskin—, (A) 683
, Impregnating—, with Solid Lubricants, J. Williamson, (P) 584
Industry, Development of—, A. H. Lockwood 35
Industry, Importance of Chemical Control in the—, M. S. Salomon and W. M. Seaber, (A) 569
Industry, Report of Research Institute for—, B. Kohnstein, (A) 125
, Machine for Brushing and Cleaning—, W. R. Smith, (P) 284
, Machine for Glazing and Graining—, A. H. Stanley, (P) 234
, Methods of Preparing Artificial—, H. Sichling, (A) 575
, Methods of Treating—, W. R. Smith, (P) 343
, Mocha—, (A) 634
, Pigskin—, (A) 635
. Process of Making Non-Slipping—. F. Kornacher, (P) 584
, Production of—, E. E. M. Payne, (P) 694
-Shaving Machines, Cylinder for—, C. A. Lougee, (P) 182
-Staking Machine, E. J. F. Quirin, (P) 584
-Splitting Machine, J. H. Gay, (P) 694
, Tawed—, (A) 181
, White Pigments for—, A. A. Claflin, (A) 274
Light Leather Liming Control, J. T. Wood and D. J. Law 346
Lime and Its Preparation, L. T. Roenitz 165
Liming, Process of—, E. Andreis 609
Liquors, Process for Clarifying Tanning—, A. Redlich, (P) 234
Mangrove Bark of North Queensland and the Manufacture of Mangrove Cutch, F. A. Coombs and G. H. Russell, (A) 273
Mangrove Barks, Results of Researches on—, Dr. J. Paessler, (A) 46
Matt Chrome Leather, Manufacture of—, (A) 336
Matter, Composition of—, A. H. Henderson, (P) 283
Meeting of British Section of I. A. L. T. C. at Leeds, May 18th, (A) 388
Methods of A. L. C. A. for 1912 52
Mineral Lubrication Oils, Manufacture of—, (A) 123
Mineral Oil in Olein, Determination of—, W. N. Chercheffsky, (A) 278
Moisture, Calcium Carbide Method for Determining—, H. C. McNeil, (A) 630
Myrobalans, C. M. Procter, (A) 632
Nitrogen, Process for Recovering—, H. L. Watrigant, (P) 583
, Simplification in the Estimation of—, R. Neumann, (A) 636
Non-tans, Value of—, in Extracts, H. C. Reed 204
, Value of—, in Tanning Materials and Extracts, J. G. Parker and J. R. Blockley 192
Oak Bark Extract, English—, (A) 390
Oil, Seal—, A. W. Hoppenstedt 13

Digitized by Google

Oil, Neats-foot—, W. Fahrion, (A) . . . 223
, Turkey Red—, F. W. Richardson and W. K. Walton, (A) . . . 229
, Tests for Linseed—, and Its Adulterants, J. S. Liverseege and G. D. Elson, (A) . . 275
Analysis, Method for—, C. Eachus . . . 552
of Mustard, Use of—. as an Antiseptic, J. M. Seltzer . . . 458
-Testing Machine, O. Stern-Sonneburn, (P) . . . 504
Oils and Fats, Discussion of Report on—, . . . 102
From Fish Refuse, Manufacture of—, V. Cambon, (A) . . . 123
, Leather Fats and--, G. Schneeman, (A) . . . 129
, Origin of Some Lubricating—, N. Chercheffsky and R. Escudie, (A) . . . 233
, Coefficient of Expansion of—, B. Kohnstein, (A) . . . 233
, Methods for Testing Lubricating—, T. D. Simpson . . . 235
, New Oxygen Absorption Method for—, L. P. Wilson and G. S. Heaven, (A) . . . 445
, Analysis of Sulphonated—, U. J. Thuau, (A) . . . 498
and Fats. Report on—, C. R. Oberfell . . . 656
Pipetting Dangerous Liquids, Device for—, L. Balderston . . . 262
P. M. C. Armstrong . . . 398
Pigskins for Saddles, Tanning and Dressing of—, G. B. Stockton, (A) . . . 176
Plumping of Hides, Notes on—, . . . 208
Potassium, Estimation of—, W. A. Davis . . . 430
Procter, Henry Richardson . . . 440
Puering, Method for the Quantative Determination of the Falling of Skins in the—, or Bating Process, H. J. S. Sand, J. T. Wood and D. J. Law . . . 253
, Process of--, Hides and Skins, H. Becker, (P) . . . 234
, Lamb Pelts, Refuse from—, G. Eberle and L. Krall, (A) . . . 129
Purification of Liquid Tannery Waste. E. C. Alsop . . . 72
Purification of Water and Sewage by Ozone, M. P. Otto, (P) . . . 393
Purging with Acetic Acid, (A) . . . 389
Quebracho Extract, Effect of Difficult Soluble Ingredients of—, upon Rendement, A. W. Moeller . . . 43
, Valuation of Cold Soluble—, W. Appelius, (A) . . . 130
Quebracho Wood and Its Substitutes, C. D. Mell and W. D. Brush . . . 481
Rawhide, Treatment of—, G. H. Henderson, (P) . . . 283
Red Mangrove Bark in Madagascar, J. G. Carter, (A) . . . 175
Reichert-Meisel Value, Estimation of—, Dr. M. Siegfeld, (A) . . . 45
Rising or Pickling of Skins, J. T. Wood . . . 409
Salt Stains, A. Jouve . . . 573
, . . . 672
, Causes of—, and Means of Avoiding Them, Rappin, T. Grosseron and L. Soubranne, (A) . . . 573
, Origin of—, G. Abt . . . 492
Salted Hides in South America, A. R., (A) . . . 180
Samples, Exact Method of Taking—, J. Paessler, (A) . . . 445
Scudding, Effect of—, on Hides and Skins, (A) . . . 228
Sewage Separator, J. S. Miller, (P) . . . 283
Sewage Sludge and Its Disposal, J. Grossman, (A) . . . 176
, Treatment of—, J. S. Waddington, (P) . . . 283
, Treating, S. H. Adams, (P) . . . 343
Skin, Method for Determination of Falling of—, H. J. S. Sand, J. T. Wood and D. J. Law . . . 253
Soap, Lime—, (A) . . . 634
Soja Bean Oil (A) . . . 124
Sole-Leather, Plumping of—, in North Germany, (A) . . . 337
, Manufacture of—, . . . 126
Splitting Leather with a Band-knife Machine, (A) . . . 214
Staking Machine, W. P. Thompson, (P) . . . 182
Stock for Leather-board Production of—, A. L. Clapp, (P) . . . 583
Suede Leather from Foreign Hides, W. Eitner, (A) . . . 178
Suede Leather, Dyeing and Currying of—, W. Eitner, (A) . . . 178

Digitized by Google

Sulphides in Lime Liquors, Estimation of--, J. R. Blockley and P. V. Mehd 358
Sulphites and Bisulphites, Process of Making Anhydrous—, E. H. Strickler, (P) . 284
Sulphite-Cellulose Extract in Leather, Detection of—, A. Gansser, (A) 635
Sulphite-Cellulose Extract, Analysis of—, F. M. Loveland 368
Sulphuric Acid in Leather, Free—, E. Stiasny and C. D. Wilkinson 461
Sumac Skivers, Blast on—, (A) 276
Swelling in Sole Leather Tannage, W. Eitner, (A) 281
Superintendents, Are Tanners Teaching Their—, How to Think? H. W. Healy . . . 31
Tannage by Means of Sallts of Cerium, F. Garelli, (A) 575
, Formaldehyde—, L. Meunier, (A) 574
for Weight, W. Eitner, (A) 44
, Theory of—, B. Kohnstein, (A) 575
, Vache Leather—, (A) 692
, Oil—, J. Lewkowitsch and J. T. Wood, (P) 694
Tanners' Problems, G. Randall, (A) 583
Tannery Liquors, Free Sulphuric Acid in—, F. O. Sprague 670
Sewage Disposal, F. A. Loveland 474
Tannic Acids, Ethyl Gallate and the Supposed Ester of Tannic Acid, H. C. Biddle and W. P. Kelly 433
Tannin Analysis, Report of Committee to Revise Wording of Official Method for . . . 287
, Methods in—, ... 91
Tannin and Synthesis of Similar Substances, E. Fischer and K. Freudenberg (A) . . 390
, Composition of—, L. F. Iljin, (A) 131
, Constitution of—, R. J. Manning and M. Nierenstein, (A) 502, 582
, M. Nierenstein, (A) 279, 579
, W. Steinkopf and J. Sargarian, (A) 131
From Chinese Gall Nuts, K. Feist and H. Haun, (A) 694
, Kohnstein's New Identification of—, L. Pollak, (A) 449
, Materials, Use of—, and Their Analysis, G. E. Knowles, (A) 391
Plants of Paraguay, W. W. Stockberger 185
? What is—, R. H. Wisdom 371
Tannins, The—, A. W. Hoppenstedt 87, 170
, Qualitative Detection and Differentiation of Vegetable—, E. Stiasny 548
, Reactions of the—, W. Eitner, (A) 230
Tanning, Applied Chemistry in the Service of—, E. Stiasny, (A) 341
, J. Forster, (P) 394
Compound, (P) 584
-drum, C. Haas, (P) 584
Effluents, Purification of—, L. Meunier, (A) 687
Experts of To-day, (A) 689
Tanning Extracts, Analysis of—, E. Schell 209
, Decolorization of—, E. Giusiana, (A) 682
, Decolorization of and Clarification of—, B. Kohnstein, (A) 575
, Process of Decolorizing and Clarifying—, (A) 636
, Notes with Regard to—, (A) 274
Tanning Industry, Russian—, J. H. Snodgrass, (A) 635
Tanning Liquors, Acidity of—, H. G. Bennett, (A) 571
, Vegetable, L. Maustetten, (A) 688
Tanning Materials and Extracts, L. Pollak, (A) 279
, Caesalpinia digyna as a—, (A) 691
, Detection of—, A. W. Hoppenstedt 664
, of Belgian Congo, A. Pirlot, (A) 681
Tanning of Gelatine and Hide, L. Meunier and A. Seyewetz, (A) 222
, Popular Illusions in Regard to—, A. A. Claflin, (A) 632
, Process of—, G. H. Lindstrom, (P) 694
School at Barcelona 681
School at Liege 334
Tan Liquors, Acidity of—, L. Balderston 665
Tanstuffs, G. Powarnin, (A) 337
Tan Yard Liquors, Acidity of—, H. G. Bennett, (A) 382, 571

Digitized by Google

Tawed Leather, (A) 181
Technical College, Leathersellers' Company's— 547
Testing Extracts with Animalized Cotton, A. Gansser, (A) 642
Tests for Vegetable Tanning Materials, B. Kohnstein, (A) 449
Thiosulphate, Sodium—, in Chrome Tannage, E. Stiasny and B. M. Das 506
Turkey Red Oil, P. W. Richardson and W. K. Walton, (A) 229
Unhairing Hides and Skins, Process of—, L. Stern, (P) 283
Vacuum Pans, Separator for—, G. M. Newhall, (P) 182
Valonia, J. G. Parker 400
Vegetable Tanning Materials, Analysis of—, H. C. Reed 307
Viscosity, Method of Measuring Absolute—, H. P. Gurney, (A) 227
Waste Sulphite Cellulose Liquors, The Tanning Properties of—, A. A. Claflin 154
Waterproofing Compound for Leather, P. F. Frost, (P) 182
Water Treatment, Permutit System of—, L. H. Harrison 423
Water Waste from Tanneries, Purification of—, W. Appelius, (A) 342

ARTICLES FROM OTHER JOURNALS

(Page numbers without titles refer to abstracts.)

Allgemeine Gerber-Zeitung,
. 449
Berichte der deutschen chemischen Gesellschaft,
. . . . . 131, 390, 502, 582
Bourse aux Cuirs de Liége,
Notes on the Plumping of Hides 208
Chemical World,
The Permutit System of Water Treatment 423
The Estimation of Potassium 430
Chemiker Zeitung,
. . . . . 45, 48, 124, 232, 636, 691
Collegium,
. . . 42, 43, 129, 222, 223, 225, 233, 263, 278, 279, 337, 340, 574, 575, 578, 497, 498, 501, 635, 642
Qualitative Detection of Tannins 548
Free Sulphuric Acid in Leather 461
Report of the International Commission on Leather Analysis 602
Der Gerber,
. . . . . 44, 178, 179, 281, 335, 341, 637, 641, 689
Gerber Courier,
. . . . . 124, 125, 126, 128, 181, 336, 337
Hide and Leather,
. . . . . 277, 633, 634, 635, 683
Journal of the American Chemical Society,
. 227
Tannic Acid, Ethyl Gallate and the Supposed Ester of Tannic Acid 433
Journal of the Society of Chemical Industry,
. . . . . 176, 229, 273, 275, 445, 636
Value of Non-tans in Tanning Materials 192
Method for Determining the Falling of Skin 253
Notes on the Estimation of Glucose in Leather 258
Preliminary Report on Light Leather Liming Control 346
Estimation of Sulphides in Lime Liquors 358
Contribution to the Chemistry of Chrome Tannage 506
Journal of Industrial and Engineering Chemistry,
. 122
La Halle aux Cuirs,
. 573
Extracts of Cellulose 373
Origin of Salt Stains 492
Leather Manufacturer,
. . . . . 125, 389

Digitized by Google

Leather Trades Review;
. . . . . 173, 390, 569, 571, 687
The Process of Liming 609
Chrome Leather 627
Salt Stains 672
Leather World,
. . . . . 176, 177, 214, 228, 276, 336, 385, 388, 391, 634, 672
Purification of Tannery Effluents 243
The Manufacture of Belting Butts 413
Le Cuir,
. . . . . 230, 445, 682
The Analysis of Tanning Extracts 209
Ledertechnische Rundschau,
. . . . . 44, 46, 124, 129, 130, 180, 342, 392, 448, 638, 639, 688, 692
Le Marche des Cuirs,
. 681
Les Matieres Grasses,
. . . . . 123, 181, 233, 278
Shoe and Leather Reporter,
. . . . . 274, 382, 444, 632, 633, 683, 685, 687
Acids in Tan Liquors 249
Tannery Sewage Disposal 474
Are You Keeping Pace With Chemistry? 607
Chrome Sole Leather 625
Tanners Year Book,
. 583
Valonia 400
Rising or Pickling of Skins 409
Soaking of Dried Hides by means of Formic Acid 467
Zeitschrift für Angewandte Chemie,
. 503

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII JANUARY, 1912 No. 1

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. RUSSELL, J. H. YOCUM, F. H. SMALL, H. T. WILSON, } . . . . . Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, 231 W. Lake Street, Chicago, Ill.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass.

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y.

ELECTIONS.

ACTIVE.

August C. Orthmann, 526 Burleigh St., Milwaukee, Wis.

Philip M. C. Armstrong, c/o Armstrong Tanning Co., Station C, Detroit, Mich.

Thomas Blackadder, c/o Smethport Extract Co., Damascus, Va.

Frank S. May, c/o G. Levor & Co., Gloversville, New York.

Charles B. Bacon, Bureau of Chemistry, Washington, D. C.

Albert L. Burwell, P. O. Box 32, Los Angeles, Cal.

Walter Petrie, c/o C. S. Hyman & Co., London, Ontario, Can.

Raymond E. Drake, 729 Boylston St., Boston, Mass.

Erwin F. Cords, 1314 State St., Milwaukee, Wis.

Digitized by Google

ASSOCIATE.

A. H. Lockwood, Lake and La Salle Sts., Chicago, Ill.
Edwin H. Bingham, c/o Jewell Belting Co., Hartford, Conn.
Otto Wigaart, 84 William St., New York.
W. B. Carter, 515 Belgravia Court, Louisville, Ky.
William R. Cox, 4027 Sheridan Road, Chicago, Ill.
James A. Connelly, Ludlow, Penna.
Thomas S. Keirnan, North Branch and Halstead Sts., Chicago, Ill.
Charles M. Procter, 225 Purchase St., Boston, Mass.
Prescott F. Wild, 425 Purchase St., Boston, Mass.
Hugh Ross, 1210 Elston Ave., Chicago, Ill.

CHANGE OF ADDRESS.

Guido C. Vogel to 409 Terrace Ave., Milwaukee, Wis.

DIED.

William M. Norris, of Princeton, N. J., Active Member, Nov. 30, 1911.
Henry Vom Berge, of Buffalo, N. Y., Associate Member, Nov. 28, 1911.

REPORT ON PROPOSED CHANGES IN METHODS.

Following is the result of the vote cast for proposed changes in methods.

"*Official Method for Tannin Analysis, Analysis of Extracts, Section 9, Non-Tannins.* Third line commencing with 'Digest' to read 'ten times' instead of 'twenty-five times.' (This refers to the proportion of water to hide powder.)"

45 votes cast, necessary for choice, 30.
"Yes" 43, "No" 2. Adopted.

"*Official Method for Tannin Analysis, Crude Materials.* To Section 4, *Extraction of Sample,* shall be added the following: 4(a) Fresh Materials, Woods and Barks, Also Spent Materials. Five hundred cc. of extractive solution shall be collected by outside condensation in approximately two hours, and the extraction continued with 500 cc. for fourteen hours longer by the process of continuous extraction with reflux condenser. The applied heat shall be such as to give by condensation, approximately 500 cc. in one and one-half hours."

44 votes cast, necessary for choice, 30. "Yes" 29, "No" 15. Rejected.

Digitized by Google

"Official Method for Tannin Analysis, Crude Materials, Section 4, Extraction of Sample." Fifth line commencing with 'At least' to be altered to read '500 cc. etc.' "

45 votes cast, necessary for choice, 30.

"Yes" 42, "No" 3. Adopted.

H. C. REED,
Secretary.

New York, Dec. 13, 1911.

EIGHTH ANNUAL MEETING.

The eighth annual Convention of the American Leather Chemists Association assembled at the Hotel Raleigh, Washington, D. C., on Thursday morning, December 7th, 1911, with President F. P. Veitch in the Chair. In spite of repeated requests at the different sessions, a number of those in attendance failed to register. The following list is therefore incomplete, but contains the names of most of those who were present at the various sessions:

Agnew, B. S., New York City; Alsop, E. C., New York City; Alsop, W. K., Ridgway, Pa.; Balderston, L., Ridgway, Pa.; Beardmore, A. O., Torrance, Acton West, Ontario, Canada; Blackadder, Thomas, Damascus, Va.; Buchanan, Wm. T., Stokesville, Va.; Byron, Walter H., Mercersburg, Pa.; Carr, Oma, Asheville, N. C.; Claflin, Alan A., Boston, Mass.; Clough, Harrison L., Boston, Mass.; Connelly, James A., Ludlow, Pa.; Cover, J. R.; Cutler, N. P., Ludlow, Pa.; Delaney, Charles R., Hanover, Pa.; Desmond, Joseph J., Corry, Pa.; Dickerson, W. H., Muskegon, Mich.; Evans, J. V. R., Sheboygan, Wis.; Faust, Thomas A., Newark, N. J.; Fox, W. A., Kenosha, Wis.; Griffith, R. W., Chicago, Ill.; Gunnison, S. Boyd, Girard, Pa.; Haley, E. J., New York City; Heald, C. E., Lynchburg, Va.; Hoppenstedt, A. W., Buffalo, N. Y.; Hurt, H. H., Covington, Va.; Kerr, George A., Lynchburg, Va.; Kistler, Sedgwick, Lock Haven, Pa.; Kretschmar, F. K., Philadelphia, Pa.; Levi, Louis E., Milwaukee, Wis.; Lockwood, A. H., Chicago, Ill.; Loveland, Frank M., DuBois, Pa.; McLaughlin, G. D., Philadelphia, Pa.; Mardick, J. R.; Merrill, Herbert C.,

Digitized by Google

Boston, Mass.; Morrison, C. M., Pine Grove, Pa.; Norris, C. W., New York City; Oberfell, Charles R., Harrisonburg, Va.; Orth, M. S., Boston, Mass.; Pierson, J. O., Buffalo, N. Y.; Procter, Charles M., Boston, Mass.; Ransom, Neale, Jersey City, N. J.; Reed, H. C., Stamford, Conn.: Rhoads, J. Edgar, Wilmington, Del.; Riker, G. A., Newark, N. J.; Roenitz, Louis T., Chicago, Ill.; Rogers, Allen, Brooklyn, N. Y.; Rogers, J. S., Washington, D. C.; Ruppenthal, K. F., New York City; Saxe, Sig., New York City; Small, F. H., Worcester, Mass.; Smoot, Chas. C., III., N. Wilkesboro, N. C.; Snell, Walter R., Richwood, W. Va.; Teas, W. H., Marion, Va.; Trostel, George M., Canton, N. C.; Veitch, F. P., Washington, D. C.; Voiges, Paul, New York City; Wild, Prescott F., Boston, Mass.; Wilson, W. F., Lynchburg, Va.; Wisdom, R. H., Stamford, Conn.; Yocum, John H., Newark, N. J.

PRESIDENT'S ADDRESS.

F. P. VEITCH.

Members of the American Leather Chemists Association:

In calling this, the eighth annual meeting, to order it is not my purpose to detain you with extended remarks. The secretary has prepared a most entertaining program for us and I trust that the reports which will be submitted and the papers read will call forth earnest discussion.

I am gratified to see so many active members present and, even more so, that those more directly connected with practical tanning work have thought it worth while to meet with us.

There are several matters concerning the work of our association to which I would call your attention. In the past the efforts of this Association have been directed chiefly to devising and improving methods for the analysis of the materials used in the tanneries. Undoubtedly in the future the Association will have to continue and even improve its work along this line, which may be called the basic purpose of the Association.

We have devised and improved a method for the analysis of tanning materials which is probably as satisfactory as we can hope a method of the kind to be. The methods for the analysis of other materials exclusive of leather itself have been

Digitized by Google

very well worked out by those interested in other fields and it seems to me that our Association can properly follow and adopt those methods with such changes are necessary to adapt them to our special purposes. In this way we can avoid unnecessary work. There are other lines of work to which I think this Association should devote more attention. We should do more constructive work. The leather making value of different tanning materials is a subject which should receive earnest attention from this Association. The effect of the several fore-tanning, tanning and finishing processes on the value of leather, the adaptability of leather to specific purposes and its durability are matters which the members of this Association are best fitted to study. The function of bacteria and molds in tanning and their proper utilization is, I feel, one of the most important subjects to which our members can direct their attention, and one from the study of which results of the greatest economic importance will be obtained.

Another very important problem, one which every tanner in the country must sooner or later face, is the proper treatment and disposal of tannery wastes in order that the health of the community and the people residing at lower levels may not be seriously affected by these wastes. As it is today, these wastes are truly wasted. They are run into streams whose lower courses may furnish the water supply of large cities. Such a condition is no longer tolerated abroad and there can be no question but that the States and general government will shortly require the abandonment of the practice now in vogue here. Indeed, several of the States have already taken steps in this direction. It behooves this Association, therefore, to be prepared at the earliest practicable moment to dispose of tannery wastes in some harmless and, if possible, profitable manner.

I believe that certain of these wastes can be made to show a profit to the tanner and there is no question but that all of them can be rendered practically harmless. I would particularly urge that all of you who are in a position to do so would give this question serious consideration. You should know the quality and nature of the waste at your tannery.

The Association has an invitation from the officers and mem-

Digitized by Google

bers of the executive committee of the 8th International Congress of Applied Chemistry to be held in New York in the early part of September, 1912, to join the Congress and take part in its proceedings. I think our Association should hold its next annual meeting in conjunction with the organic section of the International Congress, filling certain prescribed periods. We will have an opportunity to meet many of the members of the International Association of Leather Trades Chemists who will undoubtedly attend the Congress. As a matter of pride the Association should present as many papers as possible before the Congress. These papers should be based on entirely new work and as the time of the Congress is limited, only an abstract of each paper should be prepared and only the essential features of the paper presented before the Congress. Those of you who expect to present papers before the Congress should immediately communicate with Dr. Bernhard C. Hesse, 25 Broad St., New York City.

Another subject to which I would direct your attention is the JOURNAL of the Association. Our JOURNAL is, beyond a doubt, the best one published on the subject. I feel, however, that we are not properly supporting it. We are not sending to the JOURNAL enough new material, the results of our own work or experience. I feel certain that most of us could send articles to the JOURNAL without detriment to the interests of the people we represent. On the contrary, I believe that the dissemination of general information acquired by our members would benefit the tanning industry as a whole. It is not necessary that the JOURNAL articles should be confined to analytical work. The value of the JOURNAL would be greatly increased if it contained good, practical articles on the various processes of leather making, and right here I believe our good friends, the associate members and tanners, could contribute materially to the work of this Association and also advance their own interests in the industry if they would send the JOURNAL articles based on their own experience.

The Treasurer's report was then read and referred to C. W. Norris and H. H. Hurt as an auditing committee. H. C. Reed

Digitized by Google

then read the Secretary's report, including the following statistics of membership:

Total Active Members, Dec. 1, 1911		110
Total Associate Members, Dec. 1, 1911		126
Total		236
Active Members elected during the year	11	
Associate Members elected during the year	16	
Total additions	27	
Active Members resigned during year	3	
Active Members died during year	1	
Associate Members resigned during year	7	
Associate Members died during year	2	
Total losses	13	
Net gain		14

The report of the Committee on Oils and Fats followed, presented by the Chairman, C. R. Oberfell. (This report was published in the JOURNAL, Dec., 1911.) A long discussion followed.

The report of the Committee on Acidity of Tan Liquors was next presented by L. Balderston. (This report was published in the JOURNAL for Dec., 1911.)

The Secretary then read a letter from Professor Procter to the Association, which is printed in this issue, page 10. This letter called forth an extended discussion.

The convention then adjourned to 2 P. M.

Thursday Afternoon. President Veitch in the chair.

E. C. Alsop read a paper on the Purification of Liquid Tannery Wastes by Forced Oxidation. A long discussion followed.

A. W. Hoppenstedt next read a paper on Seal Oil, which is published in this number, page 13.

The next paper was by George A. Kerr and W. F. Wilson, (read by Mr. Kerr), Notes on the Determination of Acid in Chestnut Wood and Tannery Liquors. This paper was followed by discussion.

H. C. Merrill then read a paper on Colors and Their Application to Leather, which is printed in this issue, page 15.

The convention then adjourned to 10 the next morning.

Digitized by Google

Friday Morning, Dec. 8th. Vice President Griffith in the chair.

The first business was the report of the Committee on Leather Analysis, presented by Mr. Veitch. (This report was published in the JOURNAL for Dec., 1911.) A long discussion followed, mostly on the sugar determination problem.

The presiding officer then called on Mr. Veitch, as a member of the Committee on Disposal of Tannery Wastes, for a report of progress. Mr. Veitch told of some work that is being done in regard to the fertilizer value of sediment from tannery wastes, but no formal report was presented.

H. C. Reed being called on for a report from the Committee on Rapid Cooling of Tannin Solutions, gave the results of experiments showing in some cases large differences in the amount of "reds," obtained by varying the mode of dissolving the material. A long discussion on various details of the official methods followed.

C. W. Norris exhibited a bottle which he is using for samples of solid extract. It is cylindrical, with no contraction at the mouth, so that the sample after being wrapped in waxed paper may fit the bottle quite closely, thus preventing loss of moisture to the air in the bottle, and enabling the sample to be withdrawn without breaking the bottle.

The next item was a paper by C. R. Oberfell on The Composition of Leather From Different Parts of the Hide and the Importance of a Proper Sample for Analysis. (Published in this number, page 27. A brief discussion followed.

Louis T. Roenitz then read a paper on Lime and Its Preparation. Some discussion of Mr. Roenitz's paper followed. The convention adjourned to 2 o'clock.

Friday Afternoon. Vice-President Griffith in the chair.

The first item was a paper by Henry W. Healy, read by H. C. Reed, "Are Tanners Teaching Their Superintendents How to Think?" (This paper is published in the present number, page 31.

John H. Yocum then read his paper on the Characteristics and Commercial Adaptability of Hides. Mr. Yocum's paper was followed by a long discussion, chiefly on the subject of salt stains.

Digitized by Google

On motion the council was requested to appoint a committee on the salting and curing of hides.

A. H. Lockwood then addressed the convention on the Development of the Leather Industry in Relation to the World's Hide Supply. (Mr. Lockwood's paper, with a summary of the discussion which followed, is published in this issue, page 35.)

A paper from Mr. W. M. Norris on Chrome Methods had been announced for this session. Mr. Griffith announced to the Association the death of Mr. Norris at Princeton, N. J., on Nov. 30th. The secretary was directed to convey to the relatives of Mr. Norris the sympathy of the Association.

C. M. Morrison read a paper on Vegetable Tannage versus Chrome Tannage as Applied to Heavy Leather. After some discussion of Mr. Morrison's paper, the convention adjourned to 10 o'clock Saturday morning.

In the evening nearly all the members who were in Washington attended a social dinner at Harvey's cafe.

Saturday Morning, Dec. 9th. President Veitch in the chair.

A. W. Hoppenstedt read his translation of Dr. E. Stiasny's paper entitled "Application of the Law of Mass Action to Some of the Reactions of the Tanning Process."

Next Mr. Hoppenstedt presented his own paper on the Tannins, which was followed by a brief discussion.

Alan A. Claflin then read a paper on The Tanning Properties of Waste Sulphite Cellulose Extracts. An extended discussion followed, in which the main topic was the uncertainty and difficulty involved in the analysis of sulphite-cellulose extracts.

The matter of combining the next convention with the Eighth International Congress of Applied Chemistry, was discussed at some length. By an informal vote the Association signified its willingness to hold the next convention in September, 1912, in New York, at or near the time when the International Congress is in session.

The ballots for members of Council having been counted, Charles R. Oberfell and Fritz H. Small were declared elected.

The convention then adjourned.

Digitized by Google

THE MUTUAL RELATIONS OF THE A. L. C. A. AND THE I. A. L. T. C.

By Professor H. R. Procter.

I have been asked to write something for your Convention and I need hardly say that I am heartily interested in its success; but though I have a good deal of interesting scientific work in progress, I have unfortunately nothing ready for immediate publication and I do not wish to offer you any réchauffée of already published material.

If however a few remarks on the joint work of the A. L. C. A. and the I. A. L. T. C. would be of practical interest, I should be very glad to be allowed to put them before you for consideration, premising that while any suggestions I make are purely on my own responsibility, I have reason to think that, stamped with your approval, they would be favorably received on this side; and that the present time is very opportune for their consideration.

It is clear that the objects of the two Associations are identical, and that, to avoid overlapping and mutual interference, a close alliance between them is desirable; while on the other hand, absolute freedom of individual work and control must be maintained, since not only would either side bitterly resent any attempted domination of the other, but the breadth of the Atlantic and the different conditions of the two continents interpose insuperable difficulties in the way of centralization, even were it in other respects desirable.

All I therefore propose at the moment is to consider in what ways the two Associations can usefully coöperate, without in any way destroying their mutual independence; and for convenience sake to take these points under separate headings, and offer them for separate consideration.

1. *The Journals.* It is obvious that much that appears in your JOURNAL should be and is reprinted in Collegium and *vice versa*; and that many of the leading leather chemists find it necessary to be members of both Associations in order to keep posted in the advances of leather chemistry. It is clear that setting up of the same article twice is a considerable added

Digitized by Google

expense, while the cost of printing additional copies is very small. On the other hand, distance alone quite precludes the idea of a joint editorship and a common journal. I may, however, say that on this side we are much dissatisfied with our present mode of publication, which compares in appearance and convenience very unfavorably with yours, and that we are almost certain in the near future to go over to a monthly publication on the general lines of yours.

What I now suggest is that in making this change we should have the two journals absolutely uniform in size, and as far as possible in paper and type; and should enter into a mutual arrangement by which *every* member of *both* Associations should receive *both* journals, under a financial arrangement which would fairly divide the small added costs; and at the end of the year both journals could be bound as uniform volumes or even together. The fiscal arrangements of both countries render it possible to exchange such scientific printed matter duty-free, and it would be a detail for consideration whether so to arrange our dates of publication that both could be sent out under the same cover, thus probably saving postage and labor, or to forward one at the beginning and the other at the middle of the month. To compensate for the small added expense, each journal would largely widen its sphere of influence and its scientific importance; thus probably drawing contributions from sources which at present publish in other ways, and materially increasing the value of its advertisement space.

Paging, indexing, and editorship would of course remain as at present. Articles in English might appear in either journal and so leave more room for continental papers, for which our present space is too limited; and no communication would be reprinted from one to the other in its original language. though translations would be both admissible and desirable, and it would be well that both journals should join in some arrangement for effective abstracting of all papers bearing on the science of our branch.

Membership.

Assuming that some such scheme as I have outlined should be thought possible and desirable, the question would arise whether

Digitized by Google

other privileges of membership should not also be made mutual but without voting powers except at conventions or conferences. It is obviously undesirable that two separate organizations should exist on your side, and such an arrangement would obviate this; while your position would differ from that of European sections in possessing absolute autonomy, and your own separate name. In fact the relation would be purely a federal one.

Methods of Analysis and Cooperative Work.

As regards methods of analysis, it is obvious that while uniformity is desirable, there should be no compulsion; but each side should be allowed to select its own special methods, binding on its own members, while uniformity should be sought (and ultimately reached) by agreement on general principles mutually accepted by both bodies. This method has proved very satisfactory with regard to the vexed question of tannin estimation in which our methods only differ from yours in comparatively minor details, and the two will probably still further approximate; and in many other cases, where methods are still unsettled, absolutely identical prescriptions can often be agreed upon on report of joint committees; while the investigation work required can be much lightened by being shared with you by European chemists, and institutions specially equipped for it. The same argument also applies to much cooperative work, not only in testing or inventing new methods, but in increasing our very defective knowledge of the underlying principles, and even the chemical changes involved in the tanning process.

In conclusion allow me to offer my sincere congratulations, not only on the advance of leather chemistry but upon its constantly increasing appreciation by the manufacturer; a good work in which both Associations are doing their part. I am of opinion that the better our mutual understanding and the more complete our mutual organization, the more rapidly will this educative work go on.

Much discussion followed the reading of Professor Procter's paper, and a number of suggestions were made. Finally, on motion of F. H. Small, amended by J. H. Yocum's motion, the whole matter was referred to the Council.

Digitized by Google

SEAL OIL.[1]

By A. W. Hoppenstedt.

During the past year several samples of seal oil came to my attention, and these on examination proved of such interest, that I considered it of importance to call your attention to this oil and give you a short description of its characteristics and constants.

Possibly many of you are familiar with this oil, but as far as I am aware, it finds very little application in the leather industry of this country.

Seal oil is essentially a blubber oil, being obtained by steaming the blubbers of various species of seal. The crude oil, like the fish oils, deposits stearine, which is likewise removed by cold pressing. The refined oils vary in color from light yellow to dark brown and show a striking resemblance to the cod liver oils in their appearance, odor and constants.

I have here two samples of the oil, the one a high grade oil of light yellow color and known as pale seal oil, and the other a brown oil of lower grade and called straw seal oil. The prices of these oils range from about 48c per gallon for the pale oil to about 40c per gallon for the straw oil.

Of these two grades, the brown oil or straw seal oil is of the most interest to us, and this showed the following constants:

CONSTANTS OF STRAW SEAL OIL.

Specific gravity at 15.5° C	0.9230
Free fatty acids as oleic acid	11.56%
Acid value	22.99
Saponification value	192.7
Iodine value	141.3
Unsaponifiable matter	0.09%
Test with concentrated sulphuric acid	Brown
Test for menhaden oil	Reddish-yellow
Cold test	5.5° F.
Odor	Like brown cod liver oil

You will note that the constants and characteristics shown are almost identical with those given by brown cod liver oil, and that it would therefore be practically impossible to detect seal oil if used for adulterating the same. The one essential difference shown, is in the color given with concentrated sulphuric

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec. 7, 1911.

Digitized by Google

acid, where seal oil gives a brown. Besides this, the low cold test seems to be a characteristic, and I have also noted that the oil apparently contains a lipochrome which gives a reddish-pink coloration with strong mineral acids. By shaking 10 c.c. of the oil with 5 c.c. of alcohol and then with 3 c.c. of concentrated hydrochloric acid and allowing the same to separate, the alcoholic layer assumes a reddish-pink color. I have not gone deeply into this color reaction, but surmise that by proper procedure a good test might thereby be established. By treating cod liver oil in the same manner, a greenish-yellow layer is obtained.

Thus this reaction, together with the color obtained with concentrated sulphuric acid, combined with the low cold test, lends some assistance in identifying the oil.

Considering the striking similarity in the constants of the brown seal oil and the brown cod liver oil, it seemed of decided interest to determine whether the pale seal oil would correspond in like manner to the medicinal cod liver oil, for it is well known that the medicinal cod liver oil shows a considerably higher specific gravity and very much lower free fatty acids and acid value than the brown oil. The following constants were obtained on the pale seal oil:

CONSTANTS OF PALE SEAL OIL.

Specific gravity at 15 5° C	0.9253
Free fatty acids as oleic acid	0.94
Acid value	1.86

These results showed plainly that the pale seal oil agrees with the medicinal cod liver oil, and bears the same relationship, being higher in specific gravity and very low in free fatty acids and acid value.

From all the foregoing remarks, it must impress everyone that seal oil deserves a good deal of attention, and, not only as a possible adulterant of the other oils, but also as a leather oil. In Europe, the oil finds considerable application in the leather industry, and judging from the character and features of the oil which has come under my observation, I see no reason why seal oil should not make a good substitute for cod liver oil and menhaden oil in the leather industry of this country.

Digitized by Google

COLORS AND THEIR APPLICATION TO LEATHER.[1]

By H. C. Merrill.

In talking to you today about dyestuffs and their application to leather, I am going to briefly outline the different general classes of dyestuffs and the methods used in their application. Then I will consider hurriedly some of the more important kinds of leather in which the appearance of the color makes a large part of the value of the leather, for the purpose of pointing out the most successful methods of producing the best results.

Coal tar dyestuffs will be considered today under the divisions of:

Basic Dyestuffs,
Acid Dyestuffs,
Diamine or Cotton Dyestuffs,
Anthracene, Alizarine or Mordant Dyestuffs,
Dyestuffs, Diazotized and Developed on the Fibre,
Immedial or Sodium Sulphide Dyestuffs,
Dyestuffs Oxidized on the Fibre.

I have omitted entirely the dyestuffs commonly known as *Vat Colors,* as, for example, indigo or hydron blue, because they are not suitable for application to leather.

I shall also mention the dyewoods only in their capacity as mordants for basic dyestuffs and as tanning agents because their usefulness as coloring agents has been superseded by the coal tar dyestuffs, with the exception of logwood for black leather. Even logwood is fast losing its usefulness because of the acid, diamine and developed blacks which give stronger and better feeling leather.

In this talk I shall mention only names of dyestuffs made by Leopold Cassella & Co., Frankfort, Germany, because, being in their employ, I am more familiar with them and know their peculiar properties better than the dyestuffs of other manufacturers. Also the time allotted to me for this talk limits me, so that I shall only be able to mention the most important members of the various classes of dyestuffs.

[1] Read at the A. L. C. A. Convention, Washington, D. C.. Dec. 7, 1911.

Digitized by Google

Basic Dyestuffs are the most commonly used because leather was formerly made almost entirely with vegetable tanning materials. They are also entirely suitable for chrome leather after it has been properly mordanted with a vegetable tanning material.

Basic colors are best dissolved by mixing them thoroughly with cold water, and then raising to a boil with a steam jet. Cold water is best used because basic dyes often contain material which is liable to cake if the dyes are put into hot water. Auramine should not be dissolved in water over 175° F.

If the water is hard, the dyes should be wet with acetic acid before the water is added. Diamond phosphines which are not affected by the hardness of the water, may be dissolved without the addition of acetic acid.

Phosphines were formerly made by the purification of a by-product of magenta. The new phosphines like diamond phosphines are made synthetically and are much purer compounds.

Basic dyestuffs as a class are not very fast to light. Many acid, anthracene and diamine colors are much superior to basic colors in this respect. It is, however, practically impossible for the dyer of leather to secure such excellent results as are possible for the textile dyer because the tanner cannot fix his colors by boiling heat.

Phosphine, thioflavine, diamond phosphine, Bismark brown, safranine, methylene blue and new blue are the fastest to light of the basic colors.

Auramine, chrysoidine, fuchsine, methyl violet and solid green crystals are the deepest penetrating of the basic dyes.

Basic colors are much improved in their fastness to fat liquoring and finishing if after-treated with tartar emetic, potassium titanium oxalate or bichromate of potash. These salts also make the basic dyes color the leather more level if the bottom is fixed with them before dyeing.

Acid Colors are used on both vegetable and chrome tanned leather. They readily dissolve without any addition of acid. They do not require any mordant, but the depth of color is much increased by the addition of sulphuric or formic acid to the dye bath. The most level dyeings are obtained by adding the acid

Digitized by Google

towards the end of the dyeing operation. However, the use of any acid is undesirable, especially on chrome leather, if after dyeing the leather has to be fat liquored with an alkaline emulsion of oils because the acid is liable to cause greasy spots by curdling the fat liquor.

Some of the most easy levelling acid colors include acid yellow A T, orange extra, azo orseille B B, lanafuchsine S B, cyanole F F, cyanole fast green G. These colors are quite fast to light, and also very easily soluble which causes them to easily penetrate the leather and produce very level shades. They are excellent for making light pearl and ecru shades, but are not suitable for dark shades.

Fast acid yellow 3 G, milling yellow O, brilliant crocein A Z, brilliant lanafuchsine G G and B B, alizarine cyanole E F and napthol green B are extremely fast to light. Even anthracene colors are not any better for fastness to light than these colors.

Acid colors which are in most common use are Indian yellow G, orange extra, Havana brown S concentrated, scarlet E C, brilliant crocein M O O, fast red B, bordeaux, formyl violet S 4 B, water blue, brilliant milling blue B, pure soluble blue, solid blue, nigrosine, acid green, naptholamine black, napthol black and napthol blue black.

The most important of these colors is nigrosine, which is used to produce blue blacks on vegetable and chrome tanned leather for making seasons for finishing black leather, and blackings for polishing shoes.

Acid colors are used extensively on vegetable and chrome tanned leather as a bottom for basic dyes, which they precipitate, to produce full, level colors. Their greatest success in fancy shades has been in making golden brown glazed kid, where they are used on chrome tanned goat skins, bottomed with fustic and logwood.

Acid dyestuffs are not firmly fixed on the leather by any process. They have a tendency to bleed off in the fat liquor, wherein lies one of the greatest objections to their use.

Diamine Colors have secured an important place for themselves in dyeing chrome leather. They attach themselves directly on chrome leather without any mordant, but they have only a

Digitized by Google

slight affinity for vegetable leather for which reason they dye chrome leather better if it has not been retanned with any vegetable tanning agent.

Diamine colors are most readily soluble in water. Unlike basic colors they are less soluble in acid solutions and become more soluble when alkali is added to the dye bath. Because of this characteristic, chrome leather should be as nearly neutral as possible before dyeing, in order to secure level colors, and the dye bath does not need to be acidified even at the end of the dyeing operation as the colors exhaust completely, with the exception of colors dyed with very large percentage of dyestuffs.

Diamine fast yellow F F, diamine fast orange E G and E R, diamine fast brown G and R, diamine fast red 8 B L, diamine fast bordeaux 6 B S, diamine fast blue F F B, diamine fast brilliant blue R, are extremely fast to light and are equally as good as anthracene colors. Diamine catechine B, G and 3 G, diamine black B H, diaminogene extra, diamine fast red F, diamine fast yellow B are excellent dyes for chrome leather.

Diamine colors are often improved in respect to their fastness to fat liquor by an after-treatment with bichromate of potash or copper sulphate. They seem, however, to be affected detrimentally by iron salts.

Some diamine colors seem to work better in the dye bath if 2 per cent. to 3 per cent. of salt is used.

Oxy diamine blacks are the most important of the diamine colors in use. They have come into important competition with logwood and nigrosine on chrome leather only. They do not make a black as cheaply as logwood but do not make the leather as tender nor as harsh feeling as logwood. Oxy diamine black is slightly cheaper to use than nigrosine and does not bleed in fat liquor as the latter does. If these blacks are used with logwood, they give their greatest coloring power, if dyed on the leather before the logwood.

Diamine colors give excellent shades on chrome leathers which are finished without glazing on the grain or given an ooze finish on the flesh side. They are much faster to light than basic colors. When they are topped with basic dyes they produce a

Digitized by Google

combination which is fast to light and has the fullness of the basic dyes.

Anthracene or Mordant Colors have been used to some extent on chrome leather because they are the fastest colors to light which have been produced. Many of this class of colors are unsuitable because the color is not developed except at a boiling temperature, as for instance alizarine red, which is a yellow until developed by chrome at boiling temperature. Different chemicals, such as bichromate of potash and potassium titanium oxalate, have been proposed to take the place of boiling heat, but they have been only partially successful. However, some of the mordant colors develop cold, while others give shades which, though undeveloped, are useful. These colors as a class are usually dull and are much improved if topped with basic colors.

The yellow anthracene colors such as anthracene yellow B N and C are the most important of this group.

Colors Which Are Developed on the leather have become prominent of late in the coloring of black ooze which requires much fullness of color. Other developed colors could be used for other shades in which fullness would be especially desirable, but the process is quite long and tedious and does not give colors that are any faster to light than basic dyes, which are applied much more simply. They are used at present only on chrome leather. The practice of diazotizing and developing seems to increase the softness of the leather, which is particularly beneficial in making ooze leather. The process is also carried out as cold as possible, with the exception of the dyeing at the beginning, so that the leather does not undergo the risk of being damaged. The entire process will be treated fully under the subject of black ooze on chrome tanned calfskins.

Immedial Colors are dyestuffs which are soluble only in sulphide of sodium. They have never found much use on chrome or vegetable tanned leather because they had a tendency to make the leather tender. They have been recommended for dyeing oil-tanned chamois leather. For this purpose equal parts of the immedial color and sodium sulphide crystals are dissolved in boiling water. After the solution is cooled, add 1/10 of forma-

Digitized by Google

lin and 1/5 of soap. The chamois leather is drummed in this solution then re-fat liquored. These colors are very fast to washing.

Colors Produced by Oxidation on the Fibres are used for fur dyeing. For this method of coloring two chemicals ferrol B and ferrol S crystals come into extensive use. The wool or fur skins are first treated with a strong lime solution to remove the grease and dirt. Then the lime is removed and the wool or fur is treated cold with an oxidizing mordant composed of bichromate of potash, or sulphate of iron or copper and tartaric acid. The mordanting process varies with the kind of fur skin, and the shade to be obtained. Then the furs are rinsed thoroughly and dyed with ferrol B or ferrol S crystals or a mixture of them and with the addition of hydrogen peroxide, ammonia and sometimes pyrogallic acid. By varying this process, various full even shades of brown, grey and black can be very successfully obtained. The process is carried out cold so that the skins are not damaged. They also give good fastness to light.

Dyestuffs for Leather Finishes must be selected to mix properly with the other materials in the finish.

Glaze Finishes which are composed of solutions of albumen, casein, gelatin, gums, decoctions of seeds and moss, soap, oils and waxes, and alkali must be colored with acid dyes, the most important being nigrosine. Whenever the finish is alkaline, acid dyes must be used. This also applies to alkaline solutions of shellac and casein.

Shellac Solution in Alcohol must be colored with basic dyes, which are nearly all soluble in alcohol.

Collodion Varnishes are colored with cerasine colors, which are soluble in amyl acetate solutions.

Creams composed of soap creams and turpentine creams must be colored with cerasine colors, which have been treated with stearic acid.

In coloring the different kinds of leather for special purposes, if the best results are to be obtained, (1) the leather must be properly prepared to receive the dyestuff; (2) dyestuffs must be selected which are best suited to the kind of leather and for the shade to be dyed; (3) the processes, through which the

Digitized by Google

leather must pass after dyeing, must be chosen and arranged to be least injurious to the color, and produce the desired result; (4) and great care must be taken in every process.

Chrome Tanned Calfskins are finished into several fancy leathers. The most important are the boarded tan calf, chrome Russias, and OOZE in black and fancy shades. The skins for boarded tan calf and chrome Russia are selected out of the tanned condition and colored while wet. The skins for ooze are fat-liquored after tanning with an emulsion of egg yolk and flour and then dried out, after which they are sorted and colored.

The fancy ooze colors can be made by bottoming with sumac or fustic extract and some mordant like sulphate of iron, tartar emetic, or potassium titanium oxalate, then coloring with basic dyes; or by coloring with acid or diamine dyes and sometimes topping with basic dyes. Some light shades are also made with pigments. Black ooze is made with a combination of logwood, nerazine or oxy diamine black and leather black, or with a combination of developed black and leather black.

Black Ooze Calfskins can be made with developed black as follows: This process also illustrates the use of developed colors. The chrome tanned calfskins are sorted after washing out of the chrome tannage. The skins are shaved and fat-liquored thirty minutes with 5 per cent. egg yolks and 10 per cent. flour. The skins are then drained off, hung up and dried. When dry, the skins are damped in sawdust, staked and buffed. Then they are ready for coloring. The skins must be buffed very clean so that after they are colored they will not need to be buffed a second time.

The skins for dyeing are thoroughly wet up thirty minutes in a drum of water at 140° F.

First, dyed thirty minutes at 130° F. with 12½ per cent. diamine ooze black C R.

Then fixed fifteen minutes with 5 per cent. muriatic acid.

The skins are now drained off and rinsed in cold water.

Then diazotized, running first five minutes in 10% muriatic acid.

Then add and run fifteen minutes in 5 per cent. nitrite of soda.

Then the skins are drained off and washed thoroughly.

Digitized by Google

The muriatic acid is given before the nitrite of soda because the latter has an alkaline reaction, which has a tendency to wash the black from the leather before it can be diazotized. The diazotizing must be done cold so that the nitrous gas will not escape easily from the solution.

The skins are now developed fifteen minutes with
0.8% phenylene diamine dissolved with
1.6% soda ash,
and 0.2% betanaphthol dissolved with
0.2% caustic soda.

The two solutions are made separately but are mixed before giving them to the skins.

The skins are then drained off and washed and then topped with
2% leather black No. 60763
½% acetic acid.

The skins are then thoroughly rinsed off and fat-liquored forty-five minutes with
2% acid fat-liquor.

They are then dried on hooks, damped in sawdust, staked, dry-milled, and tacked out.

Chrome Russias and Tan Boarded Chrome Calf are colored in about the same manner. Tan boarded is glazed so that it is necessary to keep these colors lighter and yellower because the glazing bakes them sadder and redder. These colors are usually made with basic dyes on top of a vegetable bottom, because they give very full, even shades. Acid and diamine colors can be selected which would be much faster to light.

Basic dyes are usually applied as follows:

Skins are first neutralized 20 minutes with ½ per cent. borax and rinsed thoroughly.

Then bottom 30 minutes with 5 per cent. fustic or sumac extract.

Fix the bottom 20 minutes with ¼ per cent. tartar emetic or potassium titanium oxalate. Drain off and rinse.

Digitized by Google

Dye 30 minutes with a mixture of

Diamond phosphine G G, R, or D,
Bismark brown E E,
New blue R.

Set the dye 15 minutes with ⅛ per cent. bichromate of potash.
Drain off and rinse well.
Fat-liquor with 6 per cent. acid fat-liquor.

Chrome Tanned Goatskins are mostly finished into black or colored glazed kid, or patent kid. Black glazed kid or patent kid are colored with logwood and a mineral striker composed of an iron, copper or titanium salt, or a combination of them, and very often are topped off with nigrosine or diamine black and methyl violet. The glazed kid manufacturer is very firm in his conviction that he must have a vegetable retannage on his skins in order to obtain a good glazed finish. Nevertheless, he has been willing to compromise and has begun to use nigrosine or diamine black for a part of his logwood, because he finds that iron or similar salts will bring up a harsh grain if not used with the greatest care. Some manufacturers are now using logwood without any striker and using enough diamine black to black the skins. Much less black would be required if no logwood was used, as the logwood forms a kind of resist for the diamine black.

Golden Brown Glazed Kid is most successfully made by dyeing with acid colors on top of a vegetable bottom.

The skins are first carefully washed and neutralized. Then they are bottomed 20 minutes in a coloring drum with

2% fustic extract
⅛% logwood crystals.

Then ¾% of a mixture composed of the proper proportions

Anthracene yellow C or milling yellow O
Orange extra
Fast red B
Naphthol blue black

are added to the liquor in the drum and the skins are milled in it 30 minutes.

The skins are then drained off and fat-liquored either with acid fat-liquor or an emulsion of neatsfoot oil and egg yolk.

Digitized by Google

These colors penetrate deeply the skins and dye very level so that bright level shades are produced by glazing.

These colors are changed somewhat by the fat-liquor but are fairly fast to light.

The acid colors are sometimes topped with basic colors which makes the color much faster to fat-liquor.

Chrome Tanned Side Leather in tan, chocolate and green shades for sporting shoes is in considerable demand. They are usually neutralized and then given a retanning of 5 per cent. sumac extract, ¼ per cent. tartar emetic and 2 per cent. acid fat-liquor, and dried on hooks.

Then the skins are sorted for the different shades, wet up and sometimes retanned with 5 per cent. fustic or sumac extract, then dyed with ½ to 1 per cent. of a mixture of

Diamond phosphine G G
Diamond phosphine R
Bismark brown E E
Cerise N
Solid green O crystals.

These colors will produce any of the tan, brown, ox blood or green shades into which this kind of leather is made.

Then the color is sometimes fixed with ⅛ per cent. of bichromate of potash and fat-liquored with 4 per cent. acid fat-liquor.

The same shades can be successfully obtained with colors fast to light, as

Milling yellow O
Diamine fast orange E G
Brilliant croceine A Z
Alizarine cyanole E F
Naphthol green B

Vegetable Tanned Leathers are usually colored with basic colors, except very light pearl and ecru shades which can be dyed better with easily levelling acid dyes. The principal difference in treating the different kinds of vegetable tanned leathers, is made in the method of preparation for coloring. The dyeing operations should be carried on at about 110° F.

India tanned sheep and goat skins contain considerable grease as well as vegetable tanning material. The grease must be

Digitized by Google

removed from the surface of the leather before it can be dyed a clear, even color. This is done by washing the skins first in soda to free the grease; then retanning with sumac; then clearing with sulphuric acid; and finally the skins are rinsed with plenty of water. The skins are then colored with basic or acid dyes. The skins, to be colored black on the grain with white backs, are stained by brushing with 8 oz. leather black T B, 2 oz. acetic acid, and 2 quarts gum tragacanth solution, to 1 pail water.

Pickled sheepskins, tanned in sumac, are simply cleared with sulphuric acid and rinsed in water. Pickled sheepskins, tanned in quebracho, for fancy colors, are washed up in sumac, which is then fixed with tartar emetic.

India sheep and pickled sheepskins are colored similarly with acid and basic dyes, and can be considered together. Whenever good fastness to washing is required, the skins should be colored with basic dyes and the color set with bichromate of potash. On very light shades which must be slightly saddened, bichromate of potash should be used instead of blue or green, when possible. When full shades are made with acid dyes, such as bright reds, dyed with scarlet E C or brilliant crocein M O O, about 2 quarts of formic acid to 30 dozen skins should be added towards the end of the dyeing operation. Formic acid is generally chosen because it is quite as strong as sulphuric acid and will evaporate, while sulphuric is absolutely stable.

Dyes for ooze leather should be selected for their penetrating power.

Excellent results in coloring sheepskins can be obtained by dyeing first with acid colors, as for example, dyeing coffee shades, first with Indian yellow G; tan shades, first with orange extra; and red brown shades, first with fast brown B N, and then topping with the proper mixture of

Diamond phosphine 2995 J
Bismark brown E E
Methylene blue B B or new blue R.

The acid dyes produce an excellently level bottom for the basic dyes.

Digitized by Google

Light pearl, grey, champagne, blue and heliotrope, are most successfully obtained by easily leveling dyes, such as

Cyanole fast green G
Cyanole F F
Lanafuchsine S G and S B
Orange extra
Acid yellow A T

These dyes also give good fastness to light.

Side Leathers for Case, Bag, Strap or Shoe Leathers are most satisfactorily dyed with basic dyes. The leather is usually bark tanned. Before coloring the leather is washed in water. About 30 sides are then milled in 1 pail dry sumac for 20 minutes, and then a solution of 8 oz. tartar emetic is added and the sides milled 15 minutes longer. The skins are then drained off ready for coloring. Any of the tan, brown, Russia red and green shades can be obtained by a combination of

Diamond phosphine G G
Diamond phosphine R
Bismark brown E E
Solid green O crystals
Cerise N

For light shades 1 oz. of dyestuff to 3 sides is sufficient; for dark shades 1 oz. to a side.

After dyeing, the color should be fixed with 5 to 10 oz. bichromate of potash. This prevents the color from stripping in the fat-liquor or in an alkaline finish.

Buffed Board Tanned Sides for shoe leather are usually colored with basic dyes. When the shoemaker uses this leather, he dips it into water to soften it. Basic dyes resist the water perfectly, but acid and other dyes wash off completely.

This leather is colored on only one side, and is therefore colored on a table by hand or in a brushing machine. As basic dyes are used, coloring with a machine is not very satisfactory because the brush, which spreads the dye, also whips it and makes it foamy. Then the dye does not work evenly. It is therefore better to brush it on by hand.

The color is often mixed with gum tragacanth or some similar gum to prevent the leather from absorbing the dye too rapidly.

Digitized by Google

Some tanners mix soap and glue with the dye to save the operation of seasoning afterwards, but the soap throws the dye out of solution in a few minutes, so that it is impossible to get uniform results. The season should be applied after the skins are colored.

THE COMPOSITION OF LEATHER FROM DIFFERENT PARTS OF THE HIDE, AND THE IMPORTANCE OF A PROPER SAMPLE FOR ANALYSIS.[1]

By Charles R. Oberfell

The analysis of a leather may be of value for a number of purposes and the importance of a representative sample somewhat depends on the kind of leather under consideration, as well as the nature of the information desired from the laboratory. For illustration, if a lot of leather consists of "bellies" and it is desired to know the kind and extent of adulteration it is a simple problem to get an average sample. If the consideration is a lot of sole leather, and it is desired to know particularly the extent of the tannage the problem is complicated. Again, if the chemist in his control work in the tannery desires to know the particular stage in tanning to which the hides have progressed, the problem of an average sample is further complicated, and a representative sample is essential if he is to obtain any exact information.

This need of a representative sample from the whole hide is brought about by the variation largely in the physical nature of different parts. As is well known the fibers on the flank parts are loose and for the most part the hide is thin. Going towards the center of the "butt" or part lying over the kidneys it gradually grows thicker and firmer until in the kidney section we have the choice part of the hide. Proceeding towards the head along the backbone the structure gradually changes and when we reach the shoulder section the hide is thicker and not so firm as the butt, and this increases through the neck into the head. The result of this variation in structure is a variation

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec. 8, 1911.

Digitized by Google

in the quality of the leather. Parts thin and loose are penetrated rapidly by the tannin and consequently more thoroughly tanned, while heavier and firmer parts are less rapidly penetrated but at the same time more tannin is physically absorbed and filled in the interstitial spaces between the fibers. We have every reason for assuming that samples taken from these various sections would give different results on analysis. The same is true regarding addition of materials to gain weight. The loosely constructed parts will receive more of these materials than the firmer parts.

In order to determine the exact conditions anticipated by the foregoing reasoning I undertook a series of analyses of leather taken from the principal sections, namely, belly, shoulder and butt.

There are certain practical limitations in obtaining a sample of leather, because it would be impracticable to cut into pieces a whole hide to obtain the sample. No one would destroy so much value for this purpose. The samples analyzed were accordingly taken with the idea of getting a representative one with the least mutilation of the parts. Three tanned and finished hides trimmed into bends, shoulders and bellies were selected. From each belly a strip was taken running the whole length, approximately one inch wide, from the inside or cut edge. From each bend a strip 2 inches wide was cut on the edge lying along the back bone. From each shoulder a strip the same width on the cut edge adjoining the bends and on the neck end.

The head was neglected as it represents less than 10 per cent. of the hide.

Figure No. 1 is cut of a hide showing the parts removed for the samples.

The strips were laid off in five inch blocks, each block was numbered and the alternate blocks were taken by selecting the even numbers on one strip and the odd numbers on the next, etc. An equal amount from this sample was then finely divided as for analysis. This made a total of three samples, which were placed in air-tight jars. The analyses were conducted according to the methods of this association and the results are given in Table I.

Digitized by Google

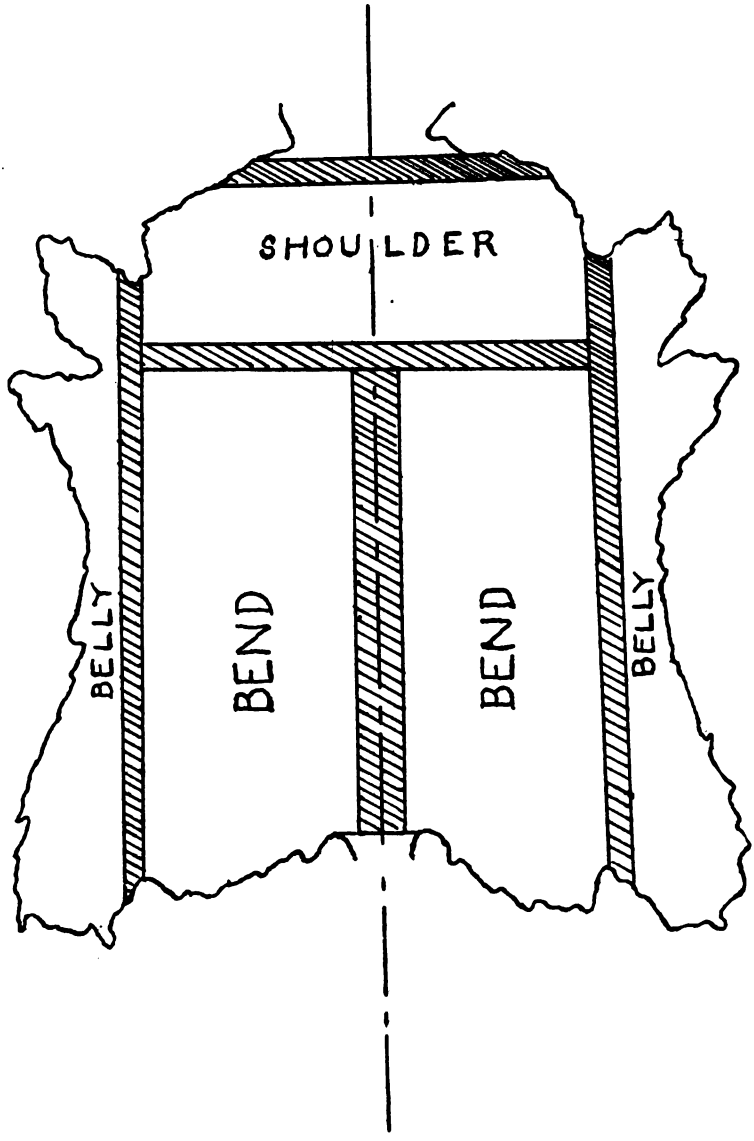


Fig. 1.

Digitized by Google

TABLE I.

	Butt	Shoulder	Belly
Moisture	13.16%	12.50%	13.15%
Oil	3.26	4.77	4.63
Uncombined tannin	17.59	19.27	17.23
Uncombined non-tannin	3.43	3.86	3.60
Combined tannin	18.21	18.83	19.23
Hide	44.24	40.67	42.05
Ash (insoluble)	0.11	0.10	0.11
Tannage number	41.2	46.3	45.7

This gives an idea of the variation likely as the leather was standard oak tanned stock.

In obtaining a representative sample of the whole hide it must be based on the relative weights of each section. In this case the shoulders averaged eight pounds, the bends ten pounds and the bellies five pounds or a total of thirty-eight pounds. Accordingly in making a composite sample fifty-three per cent. of the butt sample, twenty-one per cent. of the shoulder and twenty-six per cent. of the belly was used.

This analysis is given in Table II.

TABLE II.

	Composite sample
Moisture	12.98%
Oil	3.93
Uncombined tannin	17.69
Uncombined non-tannin	3.96
Combined tannin	18.92
Hide	42.42
Ash (insoluble)	0.10
Tannage number	44.6

In thus working for an average sample of a whole hide it will be advisable to obtain the weights of each part and when this is impossible to use average approximate weights.

An interesting comparison with the results on the composite sample in Table II is the calculated analysis from Table I made up on the same basis as the composite sample.

TABLE III.

	Composite sample	Calculated analysis
Moisture	12.98%	13.03%
Oil	3.93	3.93
Uncombined tannin	17.69	17.85
Uncombined non-tannin	3.96	3.57
Combined tannin	18.92	18.60
Hide	42.42	42.92
Ash (insoluble)	0.10	0.10
Tannage number	44.6	43.3

Digitized by Google

It appears from the results that the foregoing reasoning failed in assuming that the firmest or butt part of the hide has a greater physical absorption of tannin as indicated by the uncombined tannin results. Other assumptions as to completeness of tannage were correct, as there is a big difference between the butt and shoulder composition. There is as much as 3.57 per cent. difference in the hide, taking the two extremes and the greatest difference in the tannage number (combined tannin ÷ hide, per cent.) is 5.1 per cent. Also we notice a greater penetration of oil in the shoulder and belly sections than in the butt. This it seems would indicate, as assumed, the better penetration in these parts of any material used for false weight.

The most unlooked for result is the general agreement between the analysis of the composite sample and the belly, and this work seems to indicate that where it is impracticable to obtain a general average sample from the whole hide that it is possible to get very near the truth by taking the sample from the cut edge of the belly.

These results could have been made more conclusive by additional analyses from either heavier or lighter hides and from other tannages. However, this paper is not the result of a special investigation for that purpose, but rather the result of an investigation undertaken in the general course of my work, to determine how much variation might be expected in the composition of leather taken from the various principal parts of the hide and I trust as here presented they may prove of value to someone.

ARE TANNERS TEACHING THEIR SUPERINTENDENTS HOW TO THINK?[1]

By Henry W. Healy.

Great as has been the work done by the active members of the American Leather Chemists Association, it can only attain its true fulfillment through the intelligent coöperation of those who are largely the associate members and those under them,—the tannery superintendents. The application of the chemists' work

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec. 8, 1911.

Digitized by Google

and the suggestions for further research must come largely from those who personally make the leather, and it is indirectly, therefore, of interest to this Association that tanners be more scientifically trained in the theory of their trade. Of course, this training must largely come through the owners of tanneries or their representatives.

In spite of the progress that has been made in the methods of manufacturing leather during the past decade, it seems as if we are losing a valuable faculty that is very necessary in successfully maintaining the highest quality of leather that is consistent with a reasonably low cost of production. I might call it intelligent observation.

In former days, before the tanner had the very great help of the chemist to determine chemical values of liquors, and to assist in standardizing the proportions of their various known chemical ingredients, he had to depend upon his own faculties wholly,—the senses of taste, smell, touch and sight; in fact he had to observe closely. Very few tanners in their daily examination of their plants to-day taste liquors; the feel of leather in process is not so much depended upon to determine its condition, and too much we depend upon what the customers say in judging the quality of the finished product. With the fleshing and unhairing machines, the milling, scouring, jacking, setting and rolling machines, and with the chemists' analyses,—all valuable in progressive development,—the younger men are not developing and very naturally, perhaps, that intelligent observation upon which alone the tanner of former days had to depend for his success.

It is not difficult to produce leather at a low tannery cost, and not hard to produce a very attractive and serviceable leather if its cost were not considered; but to combine high quality and low cost requires all the tanners' art. In addition to skillful use of machines there must be intelligent interpretation and application of the chemists' analyses, but above all the condition of stock in the various stages of the tanning process must be carefully watched and compared. Only by obtaining the best conditions in the beam house, handlers and yard can the basis of the manufacture of good and cheap leather be laid.

Digitized by Google

Before the advent of chemists, machinery and subsequent improved methods, this power of intelligent observation was a tanner's only resource, gained through long and usually bitter experience. He had to have it or go to the wall, for the practical tanner was, usually at least, part owner in the business. Perhaps this contributed towards developing and sharpening this faculty. Of late modern business development has made the presence of the owner or owners of the tannery possible only part of the time, and the tanners of fifteen or twenty years ago are succeeded by men who, trained in the age of machinery, depend upon the efficacy of the bleach, the stuffing wheel and various finishing machines to produce a salable article. They understand machinery, economic factory management and the handling of labor, but have relatively little idea of how to produce the best quality and plumpness to that point where leather leaves the layaways. There must be a consistent development and growth from the soaks. This is obtained only by intelligent watchfulness and experience.

Judging from advertisements in Trade Journals for tanners and from what we constantly hear, there are more positions than good tanners to fill them. Is this not primarily the fault of the owners of the tanneries or their higher representatives? Do we take the pains to discuss with the superintendent a given condition of leather at a certain point and ask him for a logical explanation of it and then insist upon going to the elemental root of a question? Do we ask—"Why?" and again, "Why?" and insist that each answer be logical? Do we require that he must give a clearly defined reason for what exists? Of course, there are often apparent anomalies which we cannot explain, but these complexities should be resolved into their simplest terms, and by process of elimination those factors which cannot possibly be the cause should be discarded. Then the real ultimate problem can be squarely faced.

If you know, or think you know, the solution of a difficulty, make the tanner find it out for himself. Ask him what he would do, then ask why and by questioning reduce his solution either to an absurdity or show that it would be unwarrantably expensive or would have a bad ultimate effect somewhere. By

Digitized by Google

thus discarding, objecting and hinting more than likely the superintendent will hit upon the very change you have in mind. When he has done so, give him the credit of a "brand new" idea,—a discovery of his own ingenuity. He will then have added interest and apply the remedy with a sense of personal responsibility for its success. In discussing a problem, let the tanner feel that he is leading the argument and in objecting to his logic do not be destructive but give a hint at the true cause so that he will hit upon it himself a bit later. The solution will make twice the impression if he feels his own brain discovered it. When you make a change merely suggest the outline and then ask for a detailed plan for its application. Discuss each step and finally make him write the whole thing out and file the paper for future comparison. At the start most tanners write wretchedly confused and incomplete letters. This is chiefly not lack of schooling but lack of ability to think logically and coördinately. Letter writing is the greatest aid to developing analytical and logical thought.

Most of us have resorted at times to the "cut-and-try" method. But once in twenty times does it meet with any success, and then it is but temporary for there is no logical understanding of the causes of the good result:—sooner or later through modifying changes it must fail because the causes of the changes are not understood. Always have a reason for what you do and insist that the superintendent of your tannery clearly understands the logical arguments for its adoption.

Of course, the disposition of each man must be considered. Some men always think the old way is the best. Such a one must be taught that success lies with those who make progress in cheapening cost or increasing the value by taking advantage of new discoveries, and chiefly by keeping in the van by devising new ways and methods of his own. The erratic man who wants to try everything and anything must learn that the race goes not always to the swift. In short each man must be roundly developed.

Now how much time do the officers of a tanning company give to the development of their subordinates? How many think that in this lies chiefly their success? In a visit to a tannery

Digitized by Google

how much time is spent in discussing theories of tanning with the superintendent? Do we make him think that his watchfulness and intelligence are the chief factors in the success of the business? Do we realize that to the average intelligent man the hope of beating the other fellow is more than salary and that the knowledge of personal achievement is his greatest reward?

There seems to be an idea among many men that it is dangerous for a subordinate to know too much. This is a fallacy, for if the subordinate is untrustworthy he will work you harm anyway, and unless he has your confidence and you his you cannot get the full benefit of his intelligence and effort.

There is only one fundamental requisite inherently necessary to make an efficient tanner, this is faithful application,—not superficial physical activity, but genuine interest and thought. The rest is a matter of experience, growth and education. The vital spark of genuine interest in the work must first be present; the development that follows is largely under the control of the employer, and through his skillful moulding only can a good tanner be made. How many of us consider that the number of good men we have trained is the true and lasting measure of our own success?

THE DEVELOPMENT OF THE LEATHER INDUSTRY IN ITS RELATION TO THE WORLD'S HIDE SUPPLY.[1]

By A. H. Lockwood.

Two decades ago there was much discussion in the leather industry regarding the bark supply. There were predictions that hemlock bark would soon be exhausted and our low cost red sole leather would cease to be cut into cheap shoes and exported in large quantities. In those days hides and skins were in superabundant supply and such a thing as a scarcity of hides was not thought of. To-day we find these conditions reversed. The chrome tannage, quebracho and other tanning extracts successfully have reinforced the bark supply and no apprehension exists. On the other hand hides and skins appear to be decreasing steadily in quantity, as measured by demand. To those who have an aversion for statistics and remain un-

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec. 8, 1911.

Digitized by Google

convinced when long tables of figures are shown attesting that the slaughter of cattle is not keeping pace with the increase of population, the fact that hides and skins continue to advance in cost in all the markets of the world should be a demonstration of the situation.

It is sometimes alleged that there are no reliable statistics upon which to estimate the supply of hides, but the condition is neither better or worse than obtains in other world-wide commodities. There are two sets of statistics purporting to give the number of farm animals in the country. The Census Department reports once in ten years and the Agricultural Department makes an enumeration every year. The U. S. Census report was announced last month. It gave the total of range and farm cattle as 61,225,791 head against 67,719,410 for 1900—a decrease of 10.6 per cent. The population of the United States is 92,174,515 as against 75,179,940 in 1900—an increase of 21.3 per cent. It thus appears that the cattle which produce hides and the people who consume leather are numerically moving in inverse ratio. If we compare the latest Census Department figures with the Agricultural Census of 1908, a decrease of 10,041,219 head of cattle, or 14.10 per cent. is shown.

There are persons connected with the leather trade who have the Bourbon faculty of never learning, although they do forget frequently. Years ago they adopted the postulate that hides and skins are and forever must be in superabundant supply. When confronted by facts and figures such as the live stock census or the decreased slaughter of the big packers they declare that the temporary scarcity will soon right itself because more cattle will be raised.

The plain fact many times ignored is that beef has declined as a staple article of diet. Cereal breakfast foods were unknown outside of Scotland when some of us were boys. To-day, the grocer's shelves are filled with predigested stuff ranging all the way from good to bad. I venture to assert that there isn't a man in this room who has had a beefsteak for breakfast this morning. The millionaire, the chemist and the poor newspaper man are united in the modern democracy of an oatmeal, egg and grapefruit breakfast. This dietary change

Digitized by Google

is not a theory but a condition. The refrigerator car has made it possible to transport southern fruits and vegetables to northern markets and the cold storage plant enables the accumulation of fish, poultry, eggs and other food products in seasons of plenty to be dispensed during all the months of the year. The development of the poultry and egg business is remarkable. The farm animal census issued last month contained this significant clause: "Poultry shows a greater relative increase in value during the decade than the combined value of all live stock, the increase amounting to nearly $70,000,000. Poultry now are valued in this country at more than $150,000,000."

The work of the Government Bureau of Fisheries in stocking our rivers, lakes and coast waters is another important development of the food supply.

This revolution in the diet of the people under the operation of the law of supply and demand would have lowered the price of cattle at the stockyards and beef at the butchers if other circumstances had not intervened. Coincident with the decline in the per capita consumption of beef was the cutting up of the vast ranges into farms. The western semi-arid plains made economical cattle production possible. But with the settlement of the country, the cowboy and vast stretches of free grazing land are no more. Under the old system cattle were raised on the ranges and finished on corn in the middle west. One after another the cattle feeders have gone out of business. It is misleading to assume that the scarcity of cattle is only a temporary condition. Cattle raisers and feeders and the country banks which have made a specialty of cattle loans, nearly all have been obliterated by the economic change. The distribution of cattle among the states as disclosed by a census bulletin issued November 21st is a demonstration of the passing of the cattle from the ranges to the farm.

If we take nine typical range cattle states: Montana, Idaho, Wyoming, Colorado, New Mexico, Arizona, Utah, Nevada and Texas, we find they have 12,745,212 head of cattle. A comparison with nine dairy states: New York, Pennsylvania, Ohio, Indiana, Illinois, Michigan, Wisconsin, Minnesota and Iowa develops the interesting fact that these central and eastern states

Digitized by Google

have 20,643,857 head. Texas is the largest state in the union and still has the largest number of cattle—6,721,502 head or more than half the total number in the nine range states previously named. But the New England states with New York, Pennsylvania, New Jersey and Ohio have 7,402,583 head. If we take the eight range cattle states, exclusive of Texas, there are only 6,023,710 head against 6,066,278 head in New York, Pennsylvania, New Jersey and Ohio. Another astonishing contrast may be made between six central and eastern states: Illinois, Wisconsin, Minnesota, Iowa, Missouri and New York with 16,917,465 head of cattle and twelve western states: Texas, Montana, Idaho, Wyoming, Colorado, New Mexico, Arizona, Utah, Nevada, Washington, Oregon and California with only 15,734,443 head. Here we have six dairy states with 1,183,022 more cattle than twelve range states. It is also worthy of note that the western states are increasing their proportion of milch cows. Texas now has more than a million head of dairy cattle.

There is an important distinction of course between range and farm cattle as a basis of raw material for tanning. On the plains, steers are developed quickly and shipped to the feed lots for fattening when only two years old. On the farms as a rule only bull calves and worn out milch cows are sold for slaughtering. A given number of dairy cattle furnish more calfskins, but a smaller supply of hides than a similar number of animals on the ranges.

According to the year book of the Department of Agriculture there are about four hundred and fifty millions of cattle in the world, more than half of which are in North and South America. Europe and Asia each have one hundred and thirty millions and Africa and Oceania each have twelve millions. There would seem to be a basis for some sort of hide and leather Monroe doctrine concealed in the fact that there are within eighteen millions as many cattle in the Western hemisphere as in Europe and Asia combined. In so far as the leather making and consuming industries can properly take political action we should favor Pan-American reciprocity. The North and South American continents are 31.75 per cent of the

Digitized by Google

world's area, have 55 per cent of the world's supply of cattle, but have only 10.40 per cent of the world's population. With the completion of the Panama canal and the institution of closer business relations with the nations south of us, we should accept our manifest opportunity to dominate the leather industries of the world. There are millions of acres of land in Central and South America exactly suited to the raising of cattle. But the business must be exploited by capital and men from the United States, and live cattle should be put on the free list. The present duty of 27½ per cent. is practically prohibitive.

Years ago this high tariff was designed to stimulate cattle raising on our then unoccupied plains. Those who insist upon a tariff on either cattle or hides to-day are reactionary and out of alignment with modern progress.

If trade relations were cultivated with Central and South America the United States would be in a position to assume a commanding position in the leather industries of the world.

Our exports of shoes are almost equal to those of the United Kingdom, but we export twenty-eight million dollars worth of leather to Great Britain's twelve millions. With the preponderance of the hide supply on this hemisphere, and Europe, Asia and Africa demanding more leather goods, wise statesmanship would suggest a rapid expansion of our foreign traffic.

There is much evidence to show that the world, while consuming less beef per capita is demanding more leather. This seeming paradox is easily explained. There are many substitutes for beef for food, but no alternative for leather. The world could get along without the flesh of cattle, but not without the hides. The semi-civilized nations are adopting our customs of dress, especially in shoes. Since Lord Palmerston uttered his famous criticism of the Turk "What can you expect of a people who wear no heels on their shoes," slipshod methods have been corrected to some extent by the introduction of European and American styles. If the four hundred millions of people in China should demand leather shoes as a concomitant of their new government, their wants could not possibly be supplied for lack of raw material of which to make leather.

But apart from the task of civilizing the barbarous nations

Digitized by Google

with our improved footgear there is the much less remote condition at home. Our own per capita consumption of leather is increasing coincidently with our declining supply of hides and skins. Experts tell us that automobiles use two and a half hides each for their upholstering. Leather furniture is in evidence in all semi-public places and grows in favor for libraries and dining rooms in the finest homes. The late census shows a large increase of horses and mules in both number and value so that despite the automobile, harness leather will continue to be wanted in larger quantities. The Census Department's preliminary report of the trade in harness, trunks, valises, embossed leather, leather garments, etc., shows an increase in the number of establishments of 24 per cent. from 1904 and 37 per cent. increase in capital invested.

The shoe industry is not conducted with a view to economy of raw material. Durability is subordinated to style and finish. Many of the popular kinds of leather are sold without guarantee as to wear. They are beautiful but frail and use up raw material rapidly. The 1909 census of the shoe industry shows an increase of 63 per cent. in capital invested since 1904 and the gross value of product increased 43 per cent.

The importance of the goat as a leather producing animal should be considered in estimating the world's supply of raw material. Of course, goatskins are available only for light weight stock suitable for fine shoes, upholstery, fancy articles and decorations. The goat is the chief meat and dairy animal in many countries. The best available statistics tell us that there are 100,957,649 goats in the world of which less than two millions are in the United States and a little less than fourteen millions in this hemisphere. North, South and Central America have less than fourteen per cent. of the goats of the world against 55 per cent. of the beef cattle. And yet our morocco manufacturers have achieved a commanding position in the manufacture of glazed kid. They now are exporting glazed kid to the amount of about eighteen million dollars a year with what may be termed the raw material situation against them. They present an object lesson of what should be accomplished in the heavy leather trade with the preponderance of hides at hand.

Digitized by Google

Taking a broad view of the leather situation with regard to the hide supply, it would seem that future extension depends upon procuring greater quantities of raw material and developing the export trade. The day of small things in the leather industry is passing. The modern tanner must be a student of the world's markets and able to command sufficient capital to transact a greater foreign business in buying hides and skins and selling leather.

To this end we should demand a repeal of the Sherman Law and the inauguration of a Government policy designed to encourage and stimulate international trade on a large scale. It is admitted that powerful corporations are necessary properly to conduct big business. No one will object to Government control, but there is a wide difference between regulation and strangulation.

DISCUSSION.

Mr. Yocum called attention to the fact that a part of the present scarcity of hides is due to causes which we may hope are temporary, mentioning the losses in India due to the famine, in Manchuria from the war, and in South Africa due to disease. He also said that the statistics given are slightly misleading, because the average weight of animals slaughtered is increasing, so that a given percentage of decrease in numbers does not indicate so high a percentage of loss in weight of meat or of leather; the average weight of "native" hides being now six or eight per cent. higher than it was some years ago, while the dressed weight of the animals is perhaps twenty per cent. greater.

Mr. Lockwood stated that the decrease in number of cattle slaughtered had been chiefly in range cattle, whose hides are thicker than those of farm animals, and therefore more suitable for heavy leather, and expressed the belief that the average weight of hides as a whole is decreasing. He gave some figures from the Census Bureau indicating a decrease of 10 per cent. in the weight of hides taken off at 1641 establishments under government inspection, between the years 1900 and 1909. Several speakers agreed that this great reduction must be due to the inclusion in the later figures of a larger proportion of calves. Mr. Yocum reiterated his statement that while the average weight of branded hides has not changed much, "natives" have increased.

Digitized by Google

ABSTRACTS.

Chemical Investigations of the Substances in Birch. GEORG GRASSER. *Collegium*, 1911, 393-425.—Prefacing with a copious list of references to the literature of these substances, particularly betulin, tannins, tar products, gum and ethereal oils, the author describes his experiments upon the dried young leaves of Betula alba. Two kg. of these were extracted with 3 l. of boiling alcohol, this being found to be the only volatile solvent suited for extraction of the entire coloring matter. The extract was concentrated to 240 gms., and 800 cc. alcohol again added, thereby separating some insoluble material (A); the total extract was made alkaline with caustic potash. A considerable amount of solid potassium salt separated which was dissolved in 2 l. hot H_2O and acidified with H_2SO_4. The resulting ppt. was redissolved in alkali, again precipitated, and the ppt. dried and extracted with hot ether, leaving an insoluble portion (G) and yielding a difficult soluble part (E) separating on cooling; the permanently soluble part (F) is further separated by petroleum ether into insoluble (F_1) and soluble (F_2) parts. The mother liquor from the first acid decomposition of the crude potassium salt was extracted with ether yielding (C_1) and the extracted liquor was evaporated and aside from alkaline sulphate yielded to acetone insoluble (C_4) and soluble (C_5) portions. The solubilities of these various products are tabulated in great detail and based on these the author devised another method of separation represented by the scheme:

Alcohol extract + cold toluol

- easily sol. (F_2)
- insol. part + hot acetone
  - sol. part + cold $CHCl_3$
    - sol. (F_1)
    - insol. + cold ethyl acetate
      - soluble (B)
      - insol. + hot gl. acet. acid
        - soluble (C_4)
        - insoluble (C_5)
  - insol part + hot water
    - sol. + hot alcohol
      - little sol. (A)
      - easily sol. (F)
    - insol. + hot gl. acet. acid
      - easily sol. (G)
      - diff. sol. (E)

The proportions yielded were:

$$(A):(C):(G):(E):(F):(F_2):(G) = 4:6:4:1:24:20:5$$

Of these, (F_2) was characterized as a dark green wax, melting point 56°, while the other extracts were hard, brown and infusible. The substances (C_4), (C_5), (F_1) and (G) were easily soluble in alkali and the neutral solutions gave ppts. with gelatine, Br water, metallic salts, etc; they probably represent phlobaphenes of the pyrocatechin tannins. The water soluble substance (A) was defined by mineral contents, giving 4 per cent. ash (Na_2Co_3).

The substance (F_2) was best suited for investigation; 50 gms. were dissolved in dilute NH_3, precipitated with HCl and these operations re-

Digitized by Google

peated 7 times. The dried product was an asphalt like mass, melting at 62°. By combustion it analyzed $C_8H_{14}O$ and the molecular weight determination by boiling-point methods gave 615, corresponding to $C_{40}H_{70}O_5$=630. By addition of alcoholic potash to the ethereal solution and titrating back to determine carboxyl groups, it was found that 100 gms. substance required 5.80 gms. K. A similar experiment with boiling alkali required after one-half hour 12.40 gms. K. The author calls this last process the determination of a "saponifiable hydroxyl group" and deduces the formula $C_{38}H_{62}O_2(COOH)OH$ (sic). He formulated the salts $C_{37}H_{66}O_2$. $(COOK)OH$ and $C_{39}H_{62}O_2(COOK)OK$ and gives their solubilities but no analysis. Various salts containing one equivalent of metal were obtained as precipitates by double decomposition. The ethyl ester, acid chloride and amide were prepared from this resin acid (F_2) and saponification analyses of the products approximately verified the assigned formula. Dry distillation of the resin acid gave tarry and oily products with the odor of Russia leather which were not further studied. After oxidation with $KMnO_4$ in hot alkaline solution, a product was extracted with ether having the odor of butyric acid. Chromic acid proved less suitable as an oxidizing agent. On oxidation with nitric acid, the yellow extract gave a rose color with KCN, indicating picric acid and a volatile acid smelling of butyric acid; 0.2906 gm. of the silver salt of this yielded 0.1657 gm. Ag. Theory requires 0.1603 gm. for butyric acid. The conclusion is that an aromatic ring remains intact on oxidation while the side chains oxidize away. This resin acid is probably related to betulin, $C_{30}H_{50}O_2$.

W. J. K.

The Effect of Difficult Soluble Ingredients of Quebracho Extract Upon Rendement. W. MOELLER. *Collegium*, 1911, 425-6.—This communication from the laboratory of H. Renner & Co., Hamburg, sets forth the superiority of their brand of "sulphite-free" extract. This contains the phlobaphenes in colloidal solution and has not been deprived of valuable weight giving ingredients, as have clarified extracts. Three 6 per cent. liquors were compared as follows:

	I. Natural extract, filtered	II. "Sulphite-free" extract, Renner & Co.	III. "Triumph' extract, Redlich
Analysis:			
Tans	6.1	6.0	6.1
Non-tans	0.7	0.9	1.0
Tannage:			
Per cent. total tans absorbed.	59.05	65.26	52.48
Increased wt. of hide	91.91	112.65	93.16
Washing Loss:			
Per cent. tans absorbed	50.10	64.66	52.20
Increase wt. before washing	56.78	74.37	56.99
Increase wt. after washing ..	40.16	59.77	42.09

Digitized by Google

The tanning and washing experiments were made with 5 gms. hide and 125 cc. liquor; 500 cc. water were used for washing.

W. J. K.

Tannage for Weight. W. EITNER. *Gerber*, 1911, [37] 183-5.—The writer translates portions of J. H. Russell's article on "The Tannage of Heavy Leather in California," (JOURNAL, 1910, [5] 545) and remarks upon the high rendement (80 per cent. and upwards, on green weight) obtained in America as compared with results at home, where 65 per cent. is reached with difficulty. This is due to the materials and methods employed. The acid character of the hemlock employed in the Eastern States favors the tannage and it fills well. For oak, artificial acids are employed. Tannage in layers gives better yield than in drums, and prepares the hide also for weighting with dressings such as glucose and Epsom salt. One of these preparations is made in England from imported German beet-sugar. W. Neuber in Vienna makes a similar product.

W. J. K.

Preparation of Chrome Box-Calf. ("Rind-box," "vachette box.") *Leder-technische Rundschau*, 1911, No. 45.—Either green salted hides or good dry hides may be used. The former are soaked two days with frequent changes of water; the latter somewhat longer, with 1/10 per cent. caustic soda solution for the first soak. Liming is begun in a clean lime bath containing 3 per cent. Na_2S on the green weight; 2 days, hauled twice a day. The hides are transferred after draining one-half hour to a fresh lime, staying one day, hauled twice. The limes are made up with 10 per cent. lime on the green weight, and strengthened with a third as much. They are used only three times. The unhairing is done by milling with warm water. Dry hides require longer liming, and the use of arsenic. From this on the treatment of the two sorts is the same. After fleshing, if the water is hard, the hides should be drawn through a 1/40 per cent. HCl solution before graining. They are then, after washing, split on the band-knife machine, and go to the bates, which are preferably contained in wooden paddle-wheels. For 100 pounds white weight, take 8 pounds coarse wheat bran, digested at 44°C. (112°F.). Fermentation is started by adding 2 pails of old bate liquor. The hides must run easily in the paddle. The temperature after the hides are in should be about blood-heat. The paddle is run rather slowly half an hour, then stopped 2 or 3 hours, and then run ten minutes. From time to time the top hides must be pushed down, and the whole kept warm. In soft water, the process usually takes 24 hours, if the water is hard, 40. Instead of bran, any cheap kind of meal may be used, with some modifications in preparing the bate-liquor.

The pickle for 100 lbs. of white hide is made with 6 lbs. of salt and 4 gals. water. The water and hides are put into a drum. The dry salt is added and the drum run 10 minutes. Without stopping the drum, the first tan-liquor is added through the hollow axle. The liquor for 100 lbs.

Digitized by Google

hide is made by dissolving 5 lbs. chrome alum in 8 gals. hot water. In a second vessel 1¼ lbs. crystallized sal soda in 3 quarts of water. These solutions are allowed to cool to 25°C. (77°F.) and slowly mixed. The first portion of the mixture (about 6 quarts per 100 lbs. white hide) is added at about 25°C., and the drum run 10 minutes. Then another portion, 7 quarts per 100 lbs., and after 10 minutes a third portion, 9 quarts, and 10 minutes later the remaining 13 quarts are added. The drum is then run two hours. The hides are then taken out and drained. The tannage is preferably continued in vats, rather than in a drum, as this method gives fuller leather with a smoother softer feel, and also saves machinery and chemicals, since the liquors may be used over and over for a long time. The time in the vats may be 6 days, the liquors beginning at 2½° Bé., made from the used liquors of the fore-tannage strengthened with "chrome extract." The last liquor should be from 4-5° Bé. After-tannage is done in a drum, 10 gallons of vat-liquor to 100 lbs. white weight, 5 quarts of "extract" being slowly added through the axle for each 100 lbs. white weight. The drum is then run two hours. After being horsed up 12 hours they are neutralized. The "extract" is prepared by dissolving 100 lbs. chrome alum in 25 gallons of water and 100 lbs. sal soda crystals in 25 gallons of water. When both solutions are cold, the soda solution is poured into the chrome alum, a quart at a time, with continued stirring. The resulting solution is allowed to stand 24 hours, and the clear liquor drawn off from the precipitated chromium hydroxides. The precipitate is washed and dissolved in HCl; 3 lbs. glycerine are then added. The finished "extract" should show 15° to 16° Bé. L. B.

Estimation of the Reichert-Meissl Value. Dr. M. Siegfeld. *Chem. Ztg.*, 1911, No. 139, p. 1292.—Some years ago the author, in the estimation of the Reichert-Meissl value, replaced glycerin-soda lye with glycerin-potash-lye, in order to avoid the inconvenience due to the solidification of soda soap. The ease of melting and easy solubility of potash soap enabled Kreis to introduce a further improvement, a considerable reduction in the quantity of glycerin employed. He was induced to make this change by the fact that he had often found in the glycerin of commerce a not inconsiderable content of volatile fatty acid, and he could thus reduce the correction made necessary by errors introduced in that way. The author confirms this observation, remarking that samples labelled "chemically pure for analysis" gave in a blank test a Reichert-Meissl value of from 1 to 2. Kreis recommends for the saponification of 5 g. fat, 2 cc. KOH, 1:1 solution, and 4 cc. glycerin of sp. gr. 1.26. The author has used Kreis' method in a number of butter tests and found that the saponification not only proceeds smoothly but also is complete in a somewhat shorter time and can be carried out over a smaller flame. The butter samples in question had a wide range of Reichert-Meissl values. The differences lay within the customary limits.

Digitized by Google

TABLE I.

	Reichert-Meissl values			
	Customary method		Kries' method	
1 East Frisian Fall Butter	21.9	22.05	22.35	22.1
2 East Frisian Fall Butter	22.45	22.75	22.75	22.7
3 East Frisian Fall Butter	23.1	23.15	23.65	23.6
4 East Frisian Fall Butter	23.25	23.4	23.2	23.3
5 Butter from Hamelin Creamery	27.15	26.95	27.45	27.45
6 Butter from Hamelin Creamery	27.55	27.6	27.85	27.85
7 Butter from Hamelin Creamery	28.65	28.05	28.65	28.4
8 Farm Butter from Beet-Top Feeding	32.65	32.3	31.85	31.9

The end-point of the saponification is easily recognized by the ceasing of large bubbles and the formation of a thick white foam. It is not safe to take less than 4 cc. of glycerin for a butter-fat determination. In the presence of this quantity a trace of soap will sometimes solidify but as is shown in the above examples this does not hinder complete saponification. L. B.

Result of Researches on Mangrove Barks from German East Africa. DR. J. PAESSLER. *Ledertechnische Rundschau*, 1911, No. 43.—The name mangrove is applied to trees of several kinds which grow in tropical salt marshes. In all, 302 samples were received at the Freiberg Institute during 1909 and 1910. The first series of samples numbered 80. There is some uncertainty in regard to date of collection, but the author assumes they were collected during April, 1909. The second series (74 samples) are dated June, 1909; the third, (74 samples) beginning of October, 1909; the fourth, (74 samples) from the end of November, 1909, to January 1st, 1910. The samples were chiefly the barks of four species of trees, *Rhizophora mucronata, Bruguiera gymnorrhiza, Ceriops Candolleana,* and *Xylocarpus.* The samples were not only taken at different times in the year, but from trees of different ages and from different parts of the tree. Results are calculated from the air dry condition, on an assumed water content of 14.5 per cent., which is regarded as a fair average for air-dry imported barks. A general statement of results for the four kinds of bark mentioned is given in Table I.

TABLE I.

	Tannin content, per cent.		
	Lowest	Highest	Mean
Rhizophora	29.3	40.8	36.5
Bruguiera	24.8	42.3	35.8
Ceriops	24.2	32.2	25.8
Xylocarpus	26.7	32.5	29.8

The samples taken at different times of the year do not show exactly equal tannin values, but the differences observed do not point to any defi-

Digitized by Google

TABLE II.

Rhizophora. Series 3. September, 1909. Fruiting Season.

	15–20 years average sample	40–50 years average sample	80–100 years average sample	15–20 years butt sample	15–20 years middle sample	15–20 years top sample	40–50 years butt sample	40–50 years middle sample	40–50 years top sample	80–100 years butt sample	80–100 years middle sample	80–100 years top sample
Tannin	33.2	37.0	39.8	36.6	41.0	39.8	38.7	35.3	32.6	40.3	36.5	37.4
Non-tans.....	13.6	13.5	11.7	13.7	12.8	13.5	12.8	14.5	15.8	10.9	13.2	13.2
					Bruguiera.							
Tannin	33.6	35.3	40.7	31.0	21.6	21.1	42.9	44.7	39.1	43.1	40.9	41.8
Non-tans.....	12.9	12.3	12.7	13.4	11.9	13.0	9.7	10.3	9.8	10.5	11.9	11.2
					Ceriops.							
Tannin	26.2	24.2	25.6	28.0	26.7	27.8	29.9	27.2	30.6	27.1	31.5	27.7
Non-tans.....	12.0	12.7	13.1	11.0	12.0	13.1	11.6	12.4	12.7	9.4	10.2	12.4
					Xylocarpus.							
Tannin	29.3	32.5	29.0	28.0	29.1	25.7	28.3	28.8	25.8	27.1	31.8	26.5
Non-tans.....	16.1	12.8	15.1	17.2	14.9	17.2	15.5	15.1	16 0	19.1	16.0	18.9
					Rhizophora. Series 4. November.							
Tannin	34.3	38.1	40.8	34.4	36.6	31.4	31.5	36.3	33.5	36.3	41.7	39.5
Non-tans.....	13.8	12.9	13.4	12.1	14.2	13.9	13.3	13.6	14.9	14.8	13.1	14.3
					Bruguiera. December.							
Tannin	28.4	37.6	42.6	36.4	32.8	36.4	37.0	31.1	34.7	41.1	35.8	37.5
Non-tans.....	13.9	13.6	11.9	11.9	15.4	14.7	13.6	14.6	14.3	12.2	12.7	12.8
					Ceriops. November.							
Tannin	24.6	24.6	25.9	23.7	23.5	24.1	27.1	28.6	26.1	26.5	24.8	25.3
Non-tans.....	11.9	9.4	11.8	13.4	14.0	14.8	11.0	12.0	11.5	13.0	12.9	11.5
					Xylocarpus. December.							
Tannin	29.3	29.6	32.3	30.8	29.5	30.9	26.8	37.0	29.7	32.4	31.3	25.7
Non-tans.....	8.1	7.2	11.0	9.2	8.2	7.1	8.6	8.2	7.0	9.6	10.0	8.0

Digitized by Google

nite law. Results are given also for samples of bark from small branches taken at sunrise, noon, and sunset, in each series. These showed no consistent differences, and are not reproduced in table II, which includes only two of the four series. The figures in every case indicate percentages of tannin and non-tans, as found in the bark. The fruiting season for all these trees seems to extend from September to the end of the year. Table III shows average tannin values for different ages and different parts.

TABLE III.

	Average of all ages			
	Butt samples	Middle samples	Top samples	Branch samples
Rhizophora	36.8	36.8	36.1	34.2
Bruguiera	38.2	35.1	32.9	35.7
Ceriops.....	26.9	27.3	27.4	26.2
Xylocarpus	29.6	29.7	29.0	28.5

	Average of all seasons		
	15–20 years	40–50 years	80–100 years
Rhizophora	35.7	35.2	38.6
Bruguiera	33.8	36.5	37.0
Ceriops	26.1	26.5	26.9
Xylocarpus	29.5	29.5	30.7

Lactic Acid Analysis. DR. A. A. BESSON. *Chem. Zeit.*, No. 130, p. 1209, October 31, 1911.—Klapproth (*Chem. Zeit.*, 1911, p 1026,) thinks he has found two disadvantages in the author's method of experiment for obtaining exact results in work with lactic acid and its anhydrid. First the combination of the excess of free alkali with the lactic acid anhydrid is very slow, in the presence of but a small excess of alkali. Second, no figures for the excess of acid to be added were given, which is very important, for the same lactic acid boiled with 1, 2, 3 and 5 cc. of normal nitric acid gave entirely different total acid content. It will be shown below that these disadvantages do not really exist. Klapproth further maintains that in boiling an alkali solution with HCl one can avoid having some of the alkali taken up by the acid by just bringing the solution to a boil. But this is not the case, for in working out his method the author proved an excess of acid to be essential. Klapproth also criticises the author's method of preparing the solution to be analyzed. If very accurate results are to be obtained, the author of course approves of weighing the substances. For ordinary circumstances 100 cc. measured without rinsing the pipette is sufficiently accurate, especially for acids of low concentration, and in laboratories where many experiments are made daily. In order to prove that Klapproth's accusations are unjustified, the author gives figures for twenty-five experiments with lactic acid containing 72.19 per cent. free acid, 86.40 per cent. total acid, and showing an anhydride content of 13.49 per cent.

Digitized by Google

In these experiments he added excess quantities of alkali from 1½-10 cc., allowed the solution to stand cold, sometimes 5 and sometimes 10 minutes, or heating it 5 minutes on water-bath, added excess of acid from ½ to 5 cc., and then sometimes merely brought it to a boil, sometimes boiled it ½ to 2 minutes, and sometimes heated it on the water-bath 2 minutes. The greatest variation of results from 86.4 total acid content was 1.27 and the average variation only 0.1408.

From these results the author draws the following conclusions: First, in regard to the transposing of the excess of alkali with the lactic acid anhydrid; 3 cc. of excess alkali served to cause a complete transposition in ten minutes at room temperature. The transposition also takes place in a longer time with less alkali, but if the experimenter is in a hurry he can use that much without hesitation.

Second, in regard to the use of a greater or smaller excess of salt, the author proves by citing his table of results that when a reasonable amount more or less of acid is added without too great variations in concentration, and with care not to heat the solution more than to the boiling-point, no noticeable variation in result occurs.

So the author asserts that if his method is strictly followed, the faults found by Klapproth are not justified and that other methods are still more complicated and less accurate than his. E. A. B.

PATENTS.

Process for Preparation of Glue from Chrome Leather Scraps. German Patent No. 237,752. CARL SADLOW, Nagyszombat, Hungary.

The process consists in treating the finely divided scrap with caustic soda or potash at room temperature for several days, whereby the leather scrap is reduced to a structureless paste. The alkali is then neutralized by any acid. If acid is added in slight excess, the glue after drying becomes insoluble in water. The addition of an excess of alkaline carbonate renders it again soluble. The excess of salts can be washed out.—From *Haute und Leder*, Nov. 22, 1911. L. B.

Hide-Working Machine. U. S. Patent No. 1,009,734. DAVID FRIEDLANDER, Philadelphia, Pa.

Vacuum Evaporating Apparatus. U. S. Patent No. 1,009,782. CHARLES ORDWAY, New York, N. Y.

Process of Dying Hides. U. S. Patent No. 1,009,881. WILLIAM H. ALLEN, Detroit, Mich.

The process consists in stretching leather while wet on a flat plate, covering it with a porous blanket and then a sheet of wire gauze, then several other sheets of wire gauze successively coarser. These units are piled up in a room from which a part of the air is exhausted.

Digitized by Google

Fat Extraction Apparatus. U. S. Patent No. 1,010,991. HENRY L. WALTER and CHARLES E. GOODRICH, Washington, D. C.

This is an improvment of the Knorr apparatus, and is dedicated to the public. A disk and spring are arranged to hold down the material being extracted, to prevent its puffing up.

Hide-Working Machine. U. S. Patent No. 1,011,306. JOHN W. AULSON, Lynn, Mass.

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VI of the JOURNAL, for 1911, bound in cloth or half morocco, are now ready, Volumes I, II, III, IV and V in uniform binding may also be obtained. Price $6 per volume delivered. Bound volumes will be exchanged for complete sets of unbound numbers at the rate of $1.20 per volume delivered. Missing numbers will be supplied at 25 cents each. Unbound volumes for exchange should be well packed and sent to the Manager at Ridgway, Pa., expressage being prepaid at the "printed matter" rate.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII FEBRUARY, 1912 No. 2

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members. $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, 231 W. Lake Street, Chicago, Ill.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

ELECTIONS.

ACTIVE.

Louie A. Cuthbert, Ridgway, Pa.

Paul Hayes, c/o Graton & Knight Mfg. Co., Worcester, Mass.

W. A. Ostern, c/o Cassella Color Co., 182-184 Front St., New York City.

Herman G. Schanche, 3500 Gray's Ferry Road, Philadelphia, Pa.

ASSOCIATE.

Sylvan M. Barnet, Little Falls, N. Y.

Matsuo Fukushima, c/o Meiji Seikaku, Kaisha, Yayesucho Kojimachi, Tokyo, Japan.

Reinhold A. Lang, c/o Lang Tanning Co., Ltd., Berlin, Ontario, Canada.

Harry H. Smith, West Hickory, Forest County, Pa.

George W. Taylor, 119 North Fourth St., Louisville, Kv.

A. A. Whiting, 615 Oakland Boulevard, Chicago, Ill.

Digitized by Google

CHANGES OF ADDRESS.

August H. Vogel to 393 Lake Drive, Milwaukee, Wis.
Louis T. Roenitz to 217 West Lake St., Chicago, Ill.
C. F. Young should be Widdicomb Building (instead of Witticomb) Grand Rapids, Mich.
Frederick Kniffen to Room 942, Dupont Building, Wilmington, Del.
Conrad H. Propach to 400 Roslyn Place, Chicago, Ill.
Charles S. Forsyth to the Forsyth Leather Co., Wauwatosa, Wis.
August M. Kelp to 241 W. 126th St., New York City.
M. F. Nichols to P. O. Box 509, Knoxville, Tenn.
George S. Rice to Michigan Tanning and Extract Co., Petoskey, Mich.
Joseph H. Russell to 722 N. Tejon St., Colorado Springs, Colo.

METHODS OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR 1912.

METHOD FOR TANNIN ANALYSIS.

I. Crude Materials.

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

(2) *Preparation of Sample for Extraction*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of water for extraction should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be approximated as closely as practicable.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatine salt solution fails to give a precipitate. Five hundred cc. of the first portions of extractive solution should be removed and not subjected to further heating. A

Digitized by Google

thin layer of cotton must be used in order to prevent fine material passing over.

(4A) *Sumac and Kindred Materials*:

Put the material (the amount should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water and allow to soak one hour. Then extract by collecting 2,000 cc. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand over night and analyze the following day by the Official Method for Extracts.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Method for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

II. Analysis of Extracts.

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35-0.45 gram tannin per 100 cc. of solution. Dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tarred dish, evaporate and dry as directed under "Evaporation and Drying."

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir

Digitized by Google

and pour on a 590 S. & S. 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

(9) *Non-Tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with ten times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary; so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the orginal solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the filtrate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning until clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE: In order to limit the amount of dry hide powder used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 per cent. to 75 per cent. water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

Digitized by Google

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatine 10 per cent. salt solution.

(10) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

III. Analysis of Liquors.

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-Tannin*:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
0.35——0.45 gram	9——11 grams
0.25——0.35 gram	6.5—— 9 grams
0.15——0.25 gram	4——6.5 grams
0.00——0.15 gram	0—— 4 grams

Solution to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

IV. Evaporation and Drying.

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat bottomed glass dishes of not less than 2¾ inches diameter not greater than 3 inches in diameter.

Digitized by Google

V. Determination of Total Acidity of Liquors.

(17) *Reagents*:

(a) One per cent. solution of gelatine neutral to hematine. The addition of 25 cc. of 95 per cent. alcohol per liter, is recommended to prevent frothing. If the gelatine solution is alkaline, neutralize with tenth normal acetic acid and if acid neutralize with tenth normal sodium hydroxide.

(b) Hematine. A solution made by digesting hematine in cold neutral 95 per cent. alcohol in the proportion of one-half gram of the former to 100 cc. of the latter.

(c) Acid washed kaolin free from soluble matters.

(d) Tenth normal sodium hydroxide.

Directions:

To 25 cc. of liquor in a cylinder that can be stoppered, add 50 cc. of gelatine solution, dilute with water to 250 cc., add 15 grams of kaolin and shake vigorously. Allow to settle for at least 15 minutes, remove 30 cc. of the supernatant solution, dilute with 50 cc. of water and titrate with tenth normal soda using hematine solution as the indicator. Each cc. tenth normal soda is equivalent to 0.2 per cent. acid as acetic.

On public analytical work by members of this Association, the fact that the Official Method has been used, shall be so stated.

OFFICIAL METHODS FOR SAMPLING TANNING MATERIALS.

General:

Extract whether liquid or solid, and tanning materials in general all contain moisture. The amount of moisture varies with climatic conditions, but especially in liquid, and in most solid extracts become less as the extract is exposed to the air. As the value of any material shown by analysis is directly dependent upon the amount of moisture contained, and as an exposure of a comparatively few moments may alter appreciably the amount of moisture it is apparent that the sampling in all its details should be done as quickly as consistent with thoroughness and with great care to expose the material as little as possible to the air. The portions taken as samples should be placed at once into containers as nearly air-tight as possible, and preferably of glass. Wood, cardboard, poorly glazed crockery, etc., are all

Digitized by Google

porous and more or less absorbent and not suitable for retaining samples.

Liquid extract cannot be accurately sampled when it contains any frozen material. A sample of extract taken after live steam has been run into the extract has not the same concentration as the original extract. A sample of spent bark which has been standing where dust from fresh ground bark has sifted into it does not represent the degree of extraction of the spent bark. Samples of the liquor which have set around with no preservative in them for some time do not represent the condition of the liquor when sampled.

(1) *Number of Packages to be sampled*:

When carload lots, or less, of bags are to be sampled, 7 per cent. of the number of bags shall be sampled. When shipments of more than a carload and less than 2,000 bags are to be sampled, 20 bags shall be sampled. When shipments of more than 2,000 bags are to be sampled, 1 per cent. of the number of bags shall be sampled.

When 70, or less, barrels are to be sampled, 10 per cent. of the number of barrels shall be sampled. When from 71 to 140 barrels are to be sampled, 9 per cent. of the number of barrels shall be sampled. When from 141 to 210 barrels are to be sampled, 8 per cent. of the number of barrels shall be sampled. When from 211 to 280 barrels are to be sampled, 7 per cent. of the number of barrels shall be sampled. When from 281 to 350 barrels are to be sampled, 6 per cent. of the number of barrels shall be sampled. When from 351 to 420 barrels are to be sampled, 5 per cent. of the number of barrels shall be sampled. When from 421 to 500 barrels are to be sampled, 4 per cent. of the number of barrels shall be sampled. When more than 500 barrels are to be sampled, 3 per cent. of the number of barrels shall be sampled.

(2) *Liquid Extract in Barrels*:

The heads shall be removed from the number of barrels specified in (1), the contents of each barrel stirred until homogeneous, and a sample of equal size taken from each barrel. These sub-samples shall be put together in a suitable closed container and be thoroughly mixed. From this bulk duplicate samples shall be drawn for analysis. These samples shall be pre-

Digitized by Google

served in air-tight glass containers, labeled with the date of sampling and such distinguishing marks as may be necessary. When a considerable period of time is likely to elapse between the sampling and the analysis, each individual sample shall be weighed when prepared and the certified weight of the sample be marked on the label.

(3) *Liquid Extract in Bulk*:

The extract shall be agitated with air, be plunged or be mixed by some other efficient means until homogeneous. Equal samples shall then be taken from different parts of the bulk, be placed in a proper container, be thoroughly mixed and sampled as described in (2).

(4) *Liquid Extract in Tank Cars*:

The following methods are permissible:

(a) The extract shall be unloaded into clean, dry containers and sampled according to (3); or,

(b) The extract shall be mixed until homogeneous, by plunging through the dome or other effective means, then numerous equal samples shall be taken from as widely scattered parts of the bulk as possible. These samples shall then be placed in a suitable container, be mixed and sampled as in (2).

NOTE: As it is almost impossible to secure a homogeneous mixture of the extract in a tank car, this method should be used only when no other is possible. Or,

(c) The extract shall be sampled as follows while the car is being unloaded:—A quart sample shall be taken from the discharge 3 minutes after the extract has begun to run; another quart sample shall be taken 3 minutes before the extract has all run out, and three other quart samples shall be taken at equal intervals between these two. These five samples shall be transferred to a suitable container so soon as taken, be thoroughly mixed and sampled as in (2).

(5) *Solid Extracts*:

The number of packages specified in (1) shall be selected, as nearly as practicable, of equal size. Whenever possible every n^{th} package shall be set aside for sampling while the extract is being unloaded. When this is not possible, the packages shall

Digitized by Google

be selected from as uniformly distributed parts of the bulk as possible.

Samples of as nearly equal size as practicable shall be taken from each package and these samples shall represent as nearly as may be, proportionally the outer and inner portions of the extract. These sub-samples shall be placed in a clean, dry closed container. When sampling is completed, the whole composite sample shall be broken up till it will pass through a sieve of 1 inch mesh; it shall be reduced to the required bulk by successive mixings and quarterings. From this bulk duplicate samples of the required size shall be taken, be wrapped in paraffine paper, and be enclosed in the smallest clean dry air-tight glass receptacles that will hold them, labeled, etc., as in (2).

Sampling at place of manufacture shall be conducted by running a portion from the middle of each strike into a mold holding at least two pounds. These sub-samples shall be preserved with proper precautions against evaporation, and be sampled for analysis as above.

(6) *Crude Tanning Materials*:

A. Shipments in bags, mats, barrels or other similar packages.

The number of packages specified in (1) shall be emptied in uniform horizontal layers in a pile on some clean surface. At least five equal samples shall be taken from top to bottom through the pile at uniformly distributed spots. These sub-samples shall be mixed together and the bulk be reduced by mixing and quartering to the desired size. Duplicate samples of not less than two quarts each shall be preserved in air-tight containers properly labeled.

When the number of packages to be sampled is so great as to make one pile impracticable, two or more piles may be made, and the samples from the several piles properly mixed.

B. Shipments in bulk.

1. Nuts, Beans, Pods, Ground Materials, etc.

Equal portions shall be taken from at least ten uniformly distributed parts of the bulk, be mixed and sampled as in "A."

2. Bark, Wood, etc., in sticks.

Sticks shall be taken from at least ten uniformly distributed

Digitized by Google

parts of the bulk, be sawed completely through, and the sawdust thoroughly mixed and sampled as in "A."

C. Materials prepared for leaching.

Samples of equal size shall be taken at uniform intervals as the material enters the leach and be kept in a suitable container till sampling is completed. This bulk shall then be thoroughly mixed, be reduced by mixing and quartering, and duplicate samples for analysis of at least one quart in size be preserved in air-tight containers, as in "A."

(7) *Spent Material from Leaches*:

Samples of spent material shall be taken from the top, middle and bottom, and in each case from the center and outer portions of the leach. These sub-samples shall be thoroughly mixed, be reduced in bulk by mixing and quartering, and duplicate samples of at least one quart in size be preserved for analysis.

(8) *Tanning Liquors*:

The liquor shall be mixed by plunging or other effective means till homogeneous and then samples of at least one pint be taken for analysis. The addition of 0.03 per cent. of thymol or other suitable anti-ferment to the sample is essential to keep the liquor from altering its original condition.

When routine samples are taken from day to day and a composite sample analyzed, samples of equal size shall be taken from each vat after thorough mixing, be preserved in covered containers in as cool a place as possible, and be kept from fermentation by the addition of suitable anti-ferment, as above. This bulk shall be mixed till homogeneous and samples of not less than one pint each be preserved for analysis.

When a sample is taken by a member of this Association in accordance with the above method, it is requested that he state both upon the label of the sample submitted and upon the analysis blank that "this sample has been taken in accordance with the official method of sampling of The American Leather Chemists Association."

OFFICIAL METHOD FOR LEATHER ANALYSIS.

(1) *Preparation of Sample*:

The sample of leather for analysis shall be reduced to as fine

Digitized by Google

a state of division as practicable, either by cutting or grinding.

(2) *Moisture*:

Dry 10 grams of leather for 16 hours at a temperature between 95°-100° C.

(3) *Fats*:

Extract 5 to 10 grams of air-dry leather in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

(4) *Ash*:

Incinerate 10 to 15 grams of leather in a tarred dish at a dull red heat until carbon is consumed. If it is difficult to burn off all the carbon, treat the ash with hot water, filter through an ashless filter, ignite filter and residue. Add the filtrate, evaporate to dryness and ignite.

(5) *Water-Soluble Material*:

Digest 30 grams of leather in a percolator over night, then extract with water at 50° C. for three hours. The total volume of solution to be 2 liters. Determine total solids and non-tannins according to the Official Method for extract analysis.

(6) *Glucose*:

To 500 cc. of the solution obtained by extraction according to (5), add 20 cc. of normal lead acetate, shake well, let stand for an hour and filter. To 400 cc. of filtrate add dry Na_2CO_3 and filter. To the filtrate add 5 cc. concentrated HCl and boil for two hours, allowing the solution to evaporate to about 90 cc. Add dry Na_2CO_3 until the solution is about neutral, make up to 100 cc. and filter if necessary.

Take an aliquot part containing not more than 0.25 gram of sugars, add to 60 cc. of Allihn's Fehling's solution, dilute with water to 145 cc. if necessary, cover with a watch-glass, bring to boil and set in a boiling water-bath for exactly 30 minutes. Filter through an asbestos mat in Gooch crucible, wash with hot water to free from soluble salts and finally with alcohol,

Digitized by Google

dry 1 hour in water oven, cool and weigh. Multiply the weight of cuprous oxide by 0.8883 and calculate to glucose according to the following table: (Published, this JOURNAL, May, 1909, p. 125 *et seq.*, from *J. S. C. I.* **13**, 1227 *et seq.* Also printed in the Association's pamphlet.)

(7) *Nitrogen*:

Gunning modification of the Kjeldahl Method, A. O. A. C. Bulletin, No. 107 (1907).

Reagents.

Standard Acid Solutions.—Hydrochloric or sulphuric acid, the absolute strength of which has been accurately determined. For ordinary work half-normal acid is recommended. For work in determining very small amounts of nitrogen, tenth-normal is recommended. In titrating mineral acid against hydroxide solution use cochineal as indicator.

Standard Alkali Solution.—The strength of this solution relative to the acid must be accurately determined; tenth-normal solution is recommended.

Sulphuric Acid.—The sulphuric acid used should have a specific gravity of 1.84 and be free from nitrates and also from ammonium sulphate.

Sodium Hydroxide Solution.—A saturated solution of sodium hydroxide free from nitrates.

Potassium Sulphate.—This reagent should be pulverized before using.

Indicator.—A solution of cochineal is prepared by digesting and frequently agitating 3 grams of pulverized cochineal in a mixture of 50 cc. of strong alcohol and 200 cc. of distilled water for a day or two at ordinary temperature; the filtered solution is employed as indicator.

Determination.

Place 0.7 gram leather in a digestion flask. Add 10 grams powdered potassium sulphate and from 15 to 25 cc. (ordinarily about 20 cc.) of concentrated sulphuric acid. Place the flask in an inclined position and heat below the boiling-point of the acid from 5 to 15 minutes, or until frothing has ceased (a small piece of paraffine may be added to prevent extreme foaming).

Digitized by Google

Then raise the heat and boil briskly until the liquid has become quite clear and nearly colorless (the digestion should take from 4 to 5 hours).

After cooling, dilute with about 200 cc. of water. Next add 50 cc. soda solution, or sufficient to make the reaction strongly alkaline, pouring it down the side of the flask so that it does not mix at once with the acid solution. Connect the flask with the condenser, mix the contents by shaking, and distil until all ammonia has passed over into the standard acid. The first 150 cc. will generally contain all the ammonia. The operation usually requires from 40 minutes to 1 hour and a half. The distillate is then titrated with standard alkali.

Previous to use, the reagents should be tested by a blank experiment with sugar, which will partially reduce any nitrates present that otherwise might escape notice.

PROVISIONAL METHOD FOR COLOR VALUATION OF TANNING MATERIALS.

Immerse a piece of thoroughly wetted white broadcloth, three inches by four in size, in a solution of the material to be tested, containing 3 per cent. of tannin, and allow to remain with frequent agitation for 45 minutes. The solution previous to immersing the cloth is heated on a water-bath to 50° C. and the heat then turned off, the coloring being effected without a continuance of the heat. (Care must be taken that the temperature of the bath is not greater than that of the solution, *i e.*, 50° C.). The solution, in volume 250 cc. should be contained in a porcelain or glass beaker not less than 3½ inches in diameter and 4 inches deep, and the beaker immersed at least 2½ inches in the water. The bath should not be exposed to rapid cooling (5° being the usual drop) during the test. At the expiration of the time of immersion, the cloth is removed from the solution and the free coloring matter washed out thoroughly in water heated to 50° C., then well squeezed in the hand and further excess moisture removed by rolling for a minute or two in a clean towel. It is then dried smooth between pieces of blotting paper in a letter press.

Digitized by Google

PROVISIONAL METHODS FOR THE ANALYSIS OF OILS AND FATS.

Saponification Value.

Preparation of the Alcoholic KOH.—Purify the alcohol as follows: To ordinary alcohol add potassium permanganate in very fine powder or saturated solution until the pink color holds for about ten minutes; allow to stand over night, filter and distill over a fixed oil and sodium hydroxide, the first portions of the distillate, about a quarter, being rejected. Dissolve the KOH in the alcohol thus prepared, filter, and make up to half normal strength.

Determination.—Weigh off accurately in a flask holding 150-200 cc., 1.5-2.0 grams of the fat, or oil, purified and filtered if necessary. Next run into the flask 25 cc. of the alcoholic potash, attach a long cooling tube or invert condenser, and heat on the water-bath for thirty minutes, frequently imparting a rotary motion to the contents of the flask until complete solution has been effected, which can always be done unless there is considerable unsaponifiable material present. After this allow to simmer, but not to boil vigorously, for the remainder of the time. Next all 1 cc. of a 1 per cent. phenolphthalein solution prepared by dissolving 1 gram phenolphthalein in 100 cc. 90 per cent. alcohol) and titrate back the excess of potash with half-normal hydrochloric acid.

It is always best to make a blank test, treating the same amount of alcoholic potash in exactly the same manner as the solution of fat. Every source of error, as carbonic acid, etc., has therefore, as nearly as possible, the same influence on the final result, and is thus eliminated. The difference in the number of cubic centimeters of acid used for the blank test and the real test corresponds to the quantity of potash required, and is calculated to milligrams of potash to 1 gram of fat.

Acid Value.

Weigh accurately a convenient quantity of the material to be tested into an Erlenmeyer flask, and treat with about 25 cc. of a mixture of alcohol and ether, previously rendered slightly pink with alcoholic KOH after the addition of 1 cc. per cent. phenolphthalein solution. Then titrate the mixture to the same point to

Digitized by Google

which the solvent had been brought. Use tenth-normal alcoholic KOH for this and from the number of cubic centimeters required, calculate the amount of KOH absorbed. This expressed as the number of milligrams per gram of substance is the acid value.

Iodine Value.

A. O. A. C. Official Method—The Hanus Method. Bulletin No. 107.

(*a*) *Preparation of Reagents—Hanus Iodine Solution.*—Dissolve 13.2 grams of iodine in 1,000 cc. of glacial acetic acid (99.5 per cent.) showing no reduction with bichromate and sulphuric acid; add enough bromine to double the halogen content determined by titration—3 cc. of bromine is about the proper amount. The iodine may be dissolved by the aid of heat, but the solution should be cold when bromine is added.

Decinormal Sodium Thiosulphate Solution.—Dissolve 24.8 grams of chemically pure thiosulphate, freshly pulverized as finely as possible and dried between filter- or blotting- paper, and dilute with water to 1 liter at the temperature at which the titrations are to be made.

Starch Paste.—Boil 1 gram of starch in 200 cc. of distilled water for ten minutes and cool to room temperature.

Solution of Potassium Iodide.—Dissolve 150 grams of potassium iodide in water and make up to 1 liter.

Decinormal Potassium Bichromate.—Dissolve 4.9083 grams of chemically pure potassium bichromate in distilled water and make the volume up to 1 liter at the temperature at which the titrations are to be made. The bichromate solution should be checked against pure iron.

(*b*) *Determination*—(1) *Standardizing the Sodium Thiosulphate Solution.*—Place 20 cc. of the potassium bichromate solution, to which has been added 10 cc. of the solution of potassium iodide in a glass-stoppered flask. Add to this 5 cc. of strong hydrochloric acid. Allow the solution of sodium thiosulphate to flow slowly into the flask until the yellow color of the liquid has almost disappeared. Add a few drops of the starch paste, and with constant shaking continue to add the sodium thiosulphate solution until the blue color just disappears.

Digitized by Google

(2) *Weighing the Sample.*—Weigh about 0.5 gram of fat or 0.250 gram of oil[1] on a small watch crystal or in some other suitable way. Melt the fat, mix thoroughly, pour into the crystal and allow to cool. Introduce the watch crystal into a wide mouth 16-ounce bottle with ground-glass stopper.

(3) *Absorption of Iodine in Hanus Method.*—Add 25 cc. of the iodine solution to the fat or oil dissolved in 10 cc. of chloroform. Allow to stand, with occasional shaking, for thirty minutes. The excess of iodine should be at least 60 per cent. of the amount added.

(4) *Titration of the Unabsorbed Iodine.*—Add 10 cc. of the potassium iodide solution and shake thoroughly, then add 100 cc. of distilled water to the contents of the bottle, washing down any free iodine that may be noted on the stopper. Titrate the iodine with the sodium thiosulphate solution, which is added gradually, with constant shaking, until the yellow color of the solution has almost disappeared. Add a few drops of starch paste and continue the titration until the blue color has entirely disappeared. Toward the end of the reaction, stopper the bottle and shake violently, so that any iodine remaining in solution in the chloroform may be taken up by the potassium iodide solution.

(5) *Standardizing the Iodine Solution by Thiosulphate Solution.*—At the time of adding the iodine solution to the fat employ two bottles of the same size as those used for the determination for conducting the operation described under paragraphs (3), (4) and (5), but without the presence of any fat. In every other respect the performance of the blank experiments should be just as described. These blank experiments must be made each time the iodine solution is used. Great care must be taken that the temperature of the solution does not change during the time of the operation, as acetic acid and alcohol have very high coefficients of expansion, and a slight change of temperature makes an appreciable difference in the strength of the solution.

[1] Use from 0.100 to 0.200 gram in case of drying oils which have a very high absorbent of power.

Digitized by Google

Per cent. of iodine absorbed:

Weight of fat taken	1.0479	grams
Quantity of iodine solution used	40.0	cc.
Thiosulphate equivalent to iodine used	62.1	cc.
Thiosulphate equivalent to remaining iodine	30.2	cc.
Thiosulphate equivalent to iodine absorbed	31.9	cc.
Per cent. of iodine absorbed (31.9 × 0.012697 × 100) divided by 1.0479	38.65	

Unsaponifiable Matter.

Wherever possible use the following method: Saponify 5 grams, or its equivalent, with 5 cc. of a 50 per cent. by volume aqueous KOH solution and 25 cc. alcohol. Heat on the water-bath for half an hour, frequently agitating at the beginning until as complete solution has been effected as is possible. Then transfer to a shallow porcelain dish, using alcohol to rinse the flask. When the alcohol is about half evaporated off, mix 10 grams of sodium bicarbonate and 25 grams of clean quartz sand, previously washed with HCl and distilled water and dried thoroughly. Add this mixture to the soap and stir together with a glass rod. Evaporate to dryness and continue the drying for several hours or over night. The mixture is then pulverized and placed in a Soxhlet extraction apparatus, where it is extracted with a low-boiling petroleum ether for four or five hours. The ether solution, containing the unsaponifiable matter is then transferred to a separatory funnel and washed with distilled water. Then filter into a tarred flask, and distil off the solvent. The last traces may be removed by passing a current of air through the flask over the residue and finally drying in an oven at 98-100° C. for four hours. The residue is weighed as unsaponifiable matter.

For oils that cannot be treated in this way on account of their forming a glutinous mass with petroleum ether, proceed as follows:

Saponify in the same manner as above and transfer to a shallow porcelain dish. Evaporate to dryness and continue to dry for several hours, or over night, but without adding sand and sodium bicarbonate. Next add about 30 cc. petroleum ether and rub it up with the soap by means of a glass rod flattened at one end. Then decant off the ether, with whatever soap may

Digitized by Google

be in suspension in a finely divided condition and repeat the operation several times until the soap is thoroughly extracted. No less than 200 or 300 cc. in all should be used. The soap in suspension, as well as in solution is next washed out with distilled water in a separatory funnel, using a little alcohol to break up emulsions. The washing should be proceeded with cautiously at first, and the clear ether transferred to another funnel as fast as it is formed, where it may be vigorously shaken. The aqueous soap solution should also be shaken out with petroleum ether as some of the unsaponifiable matter is apt to pass into the aqueous part together with the soap. When thoroughly washed, all the ether solutions are filtered into a tarred flask, the solvent distilled off, the last traces being removed by passing a current of air through the flask and drying in the oven for four hours, as above. The residue, however, may contain small amounts of fatty acids which can be determined from the acidity and a correction made.

Maumene Test.

In a tall 100 cc. beaker weigh out such a quantity of oil as when made up to 50 grams with mineral oil will not give a rise in temperature above 60° C. Make up to 50 grams with mineral oil and place in a large beaker well lined with hair. Add 10 cc. concentrated sulphuric acid of the same temperature as the oil mixture, taking one minute to add and always allowing the pipette to drain the same length of time. Stir constantly with the thermometer during the addition of acid and continue stirring until the temperature has reached the highest point. Run blank, using the same amount of mineral oil as for test. Deduct this rise from the total rise for the mixed oil. For specific temperature, run 50 grams of water in the same way as the sample was run. Divide the rise in temperature per gram of oil by rise in temperature per gram of water and multiply the result by 100.

Specific Gravity.

Specific gravity should be determined at 20° C., both the substance and the distilled water with which it is compared being at that temperature.

Digitized by Google

Titer Test—Provisional.

A. O. A. C. Provisional Method.
Bulletin No. 107.

(*a*) *Standard Thermometer.*—The thermometer must be graduated in tenth degrees from 10° to 60°, with a zero mark, and have an auxiliary reservoir at the upper end, also one between the zero mark and the 10° mark. The cavity in the capillary tube between the zero mark and the 10° mark must be at least 1 cm. below the 10° mark, the 10° mark to be about 3 or 4 cm. above the bulb, the length of the thermometer being about fifteen inches above all. The thermometer is annealed for seventy-five hours at 450° C. and the bulb is of Jena normal 16-inch glass, moderately thin, so that the thermometer will be quick-acting. The bulb is about 3 cm. long and 6 mm. in diameter. The stem of the thermometer is 6 mm. in diameter and made of the best thermometer tubing, with scale etched in the stem, the graduation to be clear cut and distinct but quite fine.

(*b*) *Determination.*—Saponify 75 grams of fat in a metal dish with 60 cc. of 30 per cent. sodium hydroxide (36° Baumé) and 75 cc. of 95 per cent. by volume alcohol or 120 cc. of water. Boil to dryness, with constant stirring to prevent scorching, over a very low flame or over an iron or asbestos plate. Dissolve the dry soap in a liter of boiling water, and if alcohol has been used boil for forty minutes in order to remove it, adding sufficient water to replace that lost in boiling. Add 100 cc. of 30 per cent. sulphuric acid (25° Baumé) to free the fatty acids and boil until they form a clear, transparent layer. Wash with boiling water until free from sulphuric acid, collect in a small beaker, and place on the steam bath until the water has settled and the fatty acids are clear; then decant them into a dry beaker, filter, using hot water funnel, and dry twenty minutes at 100° C. When dried, cool the fatty acids to 15° or 20° C. above the expected titer and transfer to the titer tube, which is 25 mm. in diameter and 100 mm. in length (1 × 4 inches) and made of glass about 1 mm. in thickness. Place in a 16-ounce salt mouth bottle of clear glass, about 70 mm. in diameter and 150 mm. high (2.8 × 6 inches), fit it with a cork, which is perforated so as to hold the tube rigidly when in position. Suspend the thermom-

Digitized by Google

eter, graduated to 0.10° C., so that it can be used as a stirrer, and stir the mass slowly until the mercury remains stationary for thirty seconds. Then allow the thermometer to hang quietly, with the bulb in the center of the mass, and observe the rise of the mercury. The highest point to which it rises is recorded as the titer of the fatty acids.

Test the fatty acids for complete saponification as follows:

Place 3 cc. in a test-tube and add 15 cc. of alcohol (95 per cent. by volume). Bring the mixture to a boil and add an equal volume of ammonium hydroxide (0.96 sp. gr.). A clear solution should result, turbidity indicating unsaponified fat. The titer must be made at about 20° C. for all fats having a titer above 30° C. and at 10° C. below the titer for all other fats.

Melting-Point.

Take a tube of thin glass 2½ inches in length, and of such size that when the thermometer is inserted there will be about 1 mm. space between it and the glass. Fuse one end of the tube in the flame until the edges are drawn in slightly, forming a smooth, round hole. About half an inch from the other end make a small hole, either by fusing and blowing, or by filing. The tube is then ready for use. Draw a rubber band tightly over the end that was partially closed by fusion and bind on with a rubber ring. Pour such a quantity of the melted fat into the tube that when the thermometer is inserted the bulb will be a little more than covered by fat. The column of fat should then be about one and one-fourth inch in height. The thermometer, which is inserted to near the bottom on the tube is firmly secured with a perforated cork. The fat is now cooled well down below its melting-point by immersing in cold water. When this is done, take the apparatus from the cold water, remove the rubber band, and wipe dry. Then suspend the thermometer with the tube and fat attached, in an Erlenmeyer flask or other convenient air-bath, securing it by means of a cork. Place on a water-bath and as the temperature slowly rises note the point at which the fat begins to protrude quite perceptibly, also the point at which the first drop falls and the point at which the fat becomes clear. For the latter, a small cork is inserted to prevent

Digitized by Google

the fat from running out. Then remove the cork, and as the fat runs out notice its consistency, whether thin or viscous.

Cold Test—Millwood.

Warm the oil until the stearine is dissolved and filter, through several thicknesses of filter-paper, into a *dry* 4-ounce wide-mouth bottle, 1½ ounces of the oil to be tested; place in a freezing mixture and stir until the oil becomes solid, then cork and leave for one hour in the freezing mixture. Take the bottle from the freezing mixture, wipe it dry, and place in a holder of ordinary magnesia asbestos pipe covering, or any suitable holder which will insulate the sides of the bottle. The frozen oil is broken up and well stirred with the thermometer, and at every degree rise in the temperature the bottle is inverted; continue until the oil runs to the other end of the bottle. The temperature registered at this stage is to be considered the cold test.

Cloud Test—Manns.

(1) The oil must be perfectly dry, because the presence of moisture will produce a turbidity before the clouding-point is reached.

(2) The oil must be heated to 150° C. over a free flame, immediately before making the test.

(3) There must not be too much discrepancy between the temperature of the bath and the clouding-point of the oil. An oil that will cloud at the temperature of hydrant water should be tested in a bath of that temperature. An oil that will cloud in a mixture of ice and water should be tested in such a bath. An oil that will not cloud in a bath of ice and water must be tested in a bath of salt, ice and water. The test is conducted as follows: the oil is heated in a porcelain casserole over a free flame to 150° C., stirring with the thermometer. As soon as it can be done with safety, the oil is tranferred to a 4-ounce bottle, which must be perfectly dry. One and one-half ounces of the oil are sufficient for the test. A dry Fahrenheit thermometer is placed in the oil, and the bottle is then cooled in a suitable bath. The oil is constantly stirred with the thermometer, taking care not to remove the thermometer from the oil at any time during the test, so as to avoid stirring air bubbles into the oil. The

Digitized by Google

bottle is frequently removed from the bath for a few minutes. The oil must not be allowed to chill on the sides and bottom of the bottle. This is effected by constant and vigorous stirring with the thermometer. As soon as the first permanent cloud shows in the dry body of the oil, the temperature at which it occurs is noted.

With care, results concordant to within 1° Fahrenheit can be obtained by this method. The Fahrenheit thermometer is used merely because it has become customary to report results in degrees Fahrenheit. The oil must be tested within a short time after heating to 150° C. and a retest must always be preceded by reheating to that temperature. The cloud-point should be approached as quickly as possible, yet not so fast that the oil is frozen on the sides or bottom of the bottle before the cloud test is reached.

PURIFICATION OF LIQUID TANNERY WASTE BY FORCED OXIDATION.[1]

By E. C. Alsop.

A study during a number of years of the many phases of sewage disposal leads the writer to the opinion that the whole subject of such disposal may be classed under two heads, artificial and natural.

Natural disposal would include such processes as dilution, in which the waste matter is run into water, being purified by the double action of aerobic bacteria and of direct oxidation; broad irrigation, in which the waste is spread over the surface of the ground, plowed under, and consumed by plant growth; and filtration, in which the waste is clarified and to some extent purified, by mechanical adhesion to particles of sand and by the action of anaerobic bacteria.

Artificial disposal would include chemical processes, which, however, are generally not much more than precipitating actions; septic tank processes, which are concentrated anaerobic effects; and direct oxidation by forced air blasts, use of oxygen, etc.,

[1] Paper read at the A. L. C. A. Convention, Washington, D. C., December, 7, 1911.

Digitized by Google

which are nothing more than means of hurrying the natural course of events.

It would seem further that, excepting the mechanical processes in filtration and chemical precipitation, all the various processes above referred to and others may be again divided into two classes;—the action of bacteria and the action of oxygen. Indeed, it is perhaps a question if in the last analysis oxidation does not fully cover the matter, as perhaps the action of the various bacteria is nothing more or less than the bringing into intimate contact with the molecule of matter affected a tiny particle of oxygen carried by the bacterium.

For centuries the trend of development in the purification of liquid wastes has been toward those means of disposal classified above as natural, starting with the simple running off of the waste into a stream, and later on to disposal farms. Artificial disposal is of quite recent use, and all its means with few exceptions are for the forced use of bacteria.

The result is poor in the extreme. The problem of pollution of streams and contamination of domestic water supply, with resultant disease and death, has been far from reaching a practical solution; and the existing conditions are not what they should be in the present light of scientific knowledge.

The above preamble is written to indicate the frame of mind of the writer for some years, and as an introduction to the remarks pertinent to the occasion. The result of this line of thought was to turn his attention to the means of purification most neglected heretofore, the use of oxygen, and to many experiments to determine whether or not the direct contact of oxygen with wastes to be purified would give a solution of this immense problem.

The late Col. George E. Waring, in the writer's opinion the foremost American sanitary engineer, started a line of experiments in the same general direction and was particularly successful in them; but his heroic death cut short a remarkable career. It is to Col. Waring that any good resulting from this present work is due, as he was the inspiring spirit.

In 1905 the writer designed and built in San Diego, California, a septic tank with a vertical drop for the effluent, and with utili-

Digitized by Google

zation of the heat of the sun by which a current of fresh air was kept passing through the sprayed effluent. The result was a clear odorless liquid, which runs in the open gutter of a city street for a mile or more without nuisance. The reason for the lack of odor in this case is the destruction by oxidation of the animal and vegetable matter remaining in the water, after the action of the anaerobic bacteria in the tank is finished. Col. Waring erected several purification plants consisting of coke filters through which air blasts are forced; and in some of these, where conditions and proportions are correct, (as at Willow Grove Park, near Philadelphia,) the effluent is free from objection, and for the same reason, viz., the oxidation of the matter.

These results and many others of the same nature convinced the writer that he was on the right track, and he reached the general conclusion that *if oxygen is brought into intimate contact with animal or vegetable materials in a liquid state, or a very finely divided condition in suspension in water the result is the destruction of the material* into gases with a small mineral residue; and he endeavored to conduct experiments to prove the truth of this conclusion.

Until about a year ago the writer had no particular idea of applying this system to refuse from tanneries; but a visit to the Chemist of one of the large tanning companies of Pennsylvania, started the thought that if the conclusions stated above were correct, the evils of the present methods of tannery waste disposal could be terminated. In pursuance of this thought, barrels of liquid waste were sent from two tanneries of a sole leather company and from a tannery of a company making upper leather, to a concern engaged in the manufacture of apparatus for the generation of ozone, and experiments were conducted for six months or more. The line of experimentation was, first, to demonstrate that all organic matter would be consumed by oxygen; and second, to determine whether or not the system could be made commercially practicable as applied to the purification of tannery wastes.

The use of ozone in these experiments was determined on after considerable thought, as not only the most efficient means of applying oxygen to the wastes on account of the extreme chemical

Digitized by Google

activity of ozone but also because it appeared to be the cheapest method of securing the action of the oxygen.

The result of these experiments is that it has been scientifically proved that ozone in the proper amount will destroy all material of animal or vegetable nature with which it comes into intimate contact; and that the cost of the operation is economical from a commercial point of view.

The essentials in a successful purification plant of the nature indicated by this line of experiments are a separation of solids and liquids, and the mechanical apparatus necessary to bring about an absolute contact between each molecule of liquid and ozone in the correct quantity.

To secure the separation of the solids from the liquids either precipitation tanks, settling basins or centrifugal separators may be used. The best plan is the use of continuous centrifugal separators, which gives perfect control of odors, and by which the solids can be placed in receptacles for incineration, for chemical treatment to recover ammonia, greases, etc., or for drying for use as fertilizers. It was not considered a part of the purification plan to determine a value for the solids, that coming directly under the scope of the tannery chemist's work.

The liquid waste, after the solids have been removed, is run through ozone atomizers in a spray tower, falling on coke filters through which currents of ozone-charged air are continually passing, as it has been found that the action of the ozone causes a slight precipitation. The coke must be occasionally replaced, but the used coke can be burned with small loss.

The effluent resulting from this treatment is entirely unobjectionable from a sanitary standpoint, and is to all intents and purposes odorless and pure. Fish placed in it live longer than in ordinary hydrant water, and it is so nearly colorless that its presence in a pure mountain stream could not be noticed at the place where it was discharged.

While the odor and appearance of the effluent are essential to the layman, they are inferior in importance, to the sanitary engineer or to boards of health, to the bacteria content. Many cultures from the purified effluent give the maximum of bacteria per cc. as twenty-two (22), while many examinations fail to

Digitized by Google

show even one living organism. A general average of the work shows a percentage of reduction in the number of bacteria in the raw waste to the number in the purified effluent of 99.99999; that is, one bacterium remains from each ten million present in the raw waste. In no case was any pathological bacterium found.

The general results of the experiments are, then, that the wastes from three different tanneries have been treated by this system and have been rendered odorless, colorless and bacterially harmless.

But while these results are important, the commercial side of the question has been kept steadily in view, and accurate accounts of consumption of electric current and of other expenses have been kept. The result is the satisfactory solution of the second aim of the experiments, and it can be set down as a safe outside figure that the cost of the treatment will in no case exceed, with all expenses of every kind, ten cents per one thousand gallons of effluent. It is probable that the gentlemen of this association will be able to save from the solid residue, more than enough to pay all operating costs.

The cost of installation, on account of the delicate mechanism of the ozone-producing electrical apparatus, and the extreme nicety of the continuous centrifugal separator, may be higher than at first would be thought necessary, but it should be in no way prohibitory; and the results should be so nearly perfect as to justify first class installation.

It is the opinion of the writer that a solution of the tannery waste problem has been found which is commercially economical and scientifically correct.

Discussion.

Mr. Alsop showed samples of effluent raw, and the same after being purified by the process described.

Mr. Yocum suggested that tannery, wastes might perhaps be purified more completely and economically by treating the different effluents, such as limes, tail liquors and soaks, separately.

Mr. Alsop replied that his experiments indicated that the mixed effluents could be treated with entire success and that

Digitized by Google

the same process is equally applicable to sewage. The effect seems to be similar to that brought about by anaerobic bacteria in "septic tanks," but is both more rapid and more complete. For the most satisfactory results, the liquids treated by the ozone process should be nearly neutral.

NOTES ON THE DETERMINATION OF ACIDS IN CHESTNUT WOOD AND TANNERY LIQUORS.[1]

By George A. Kerr and W. F. Wilson.

The following notes are submitted with the express purpose of bringing before the Association the necessity for further research and investigation of means for identifying and estimating the acids in tanning and extract liquors.

It will scarely be gainsaid that the results obtained by methods at present countenanced here are not susceptible of intelligent interpretation, nor do they yield much information which can be utilized in practice by the tanner or extract maker. To return an acid calculated to acetic acid, as is common, may serve some useful purpose so far as denoting an increase or decrease of acidity in a given part of the yard, but, so far as indicating the beneficent or deleterious character of these acids, the existing methods are of no value.

In the case of the extract manufacturer, whose problems in acids are just being recognized, our experience shows that they are not at all applicable, and we believe the time has about arrived when both extract maker and tanner will demand more than a mere estimation of the tannin and non-tannin in the tanning materials they handle and, in addition to checking the accuracy of an invoice, will want to know in greater detail their full value in the tan yard.

Up to this time the tanner has derived much greater benefits from chemistry than the extract maker, but even then it is surprising that he has not insisted upon a further knowledge of the tanning materials, which are with pelt the fundamental basis of his product, for it must be admitted that tannery methods as

[1] Paper read at the A. L. C. A. Convention at Washington, D. C., Dec. 7, 1911.

Digitized by Google

applied to the use and blending of various materials are still largely of the rule of thumb variety.

This applies to a greater extent to the extract maker, who, in America at least, has little to show for his investment in chemistry, if we exclude the benefits from what more properly belongs to the domain of chemical engineering. It is true, perhaps, he has gained a more accurate gauge of the monetary value of a tank of extract as governed by its tannin contents, but this is about the only score to the credit side of the ledger.

The besetting weakness of the American tannery or extract factory laboratory is its adherence to routine work, the importance and value of which is much over-estimated by both tanner and chemist at this stage of knowledge and, until a reasonable period of time is set aside for research and experimentation in every laboratory, progress is going to be extremely slow, and I hope the tanners here to-day will bear this in mind.

In approaching a discussion of this kind, we are fully aware of the complexity of the subject and the difficulties surrounding elucidation. However, a start has to be made somewhere and, although we believe we have a reasonably clear idea of the end to be attained, we appreciate we have most probably followed in this preliminary work the line of least resistance; hence these notes are not to be construed as proposed methods or in any manner final, but rather as an attempt to find a starting point for further research.

The prime object of determining the acid contents of a tanning liquor is to ascertain the neutralizing, solvent and hide plumping values of the acids contained therein and, although many methods have been proposed and some accepted as workable, the authors of them do not seem to have given sufficient consideration to the character of the various acids composing the so-called total acidity, nor have they made sufficient investigation of their reactions and those of the salts invariably present in the liquors relative to the method they were endeavoring to work out, nor the effect of the acids upon the pelt itself.

We believe it is generally accepted that at least four acids are commonly found in a free state in tanning liquors, viz.; acetic, gallic, lactic and sulphuric. As to three of these, we are sure

Digitized by Google

of their presence, but the general presence of lactic acid does not seem to have been well demonstrated, nor has it been shown that the above included all the acids and we suspect very much that there are still other acids to be accounted for.

None of the American methods now employed have taken full cognizance of the mixture of acids they were employed to determine, the dominant idea apparently being to find some means of obtaining concordant or comparative results, coupled perhaps with rapid execution, ignoring the fact that, when obtained, they were indicative of nothing in particular, for, unless the proportions of the mixture of acids are shown, interpretation is impossible.

If the acids usually present in tan liquors possessed the same general characteristics and properties, some of the present methods would probably give results which could, in a rough way, be utilized for factory control, but, as they are dissimilar in many essentials, any determination arrived at volumetrically, by means of a single indicator, must perforce fail to give the information necessary to control the acidity of the yard.

This seems evident from the following examples of analysis of liquors compared with the results obtained by the hematin-gelatine method, which we adopted for comparative purposes on account of its concordance and not because we wish to discuss it specifically.

NUMBER ONE CHESTNUT WOOD LIQUOR FROM LEACHES.

S. G. 1.012. Expressed in cc's of N/10 NaOH.

Volatile acid	Gallic acid	Residual acid	Total	Indicator
9.1	9.37	10	28.47	Hematein
12.2	19.74	10	41.94	Phenolphthalein
Total acidity by the gelatine-hematein method			36.25	

NUMBER TWO CHESTNUT WOOD LIQUOR FROM LEACHES.

S. G. 1.012. Expressed in cc's of N/10 NaOH.

Volatile acid	Gallic acid	Residual acid	Total	Indicator
9.4	11.2	18.0	38.6	Hematein
14.6	19.6	18.0	52.2	Phenolphthalein
Total acidity by the gelatine-hematein method			46.0	

Digitized by Google

These figures are obtained from liquors in their simplest form, *i. e.*, fresh leach liquors, which do not possess so many of the complications involved in tan-yard liquors but, as the analysis shows, they contain a mixture of acids, the proportion of which it is necessary to be informed upon before they can be intelligently considered as tanning agents.

By the hematein-gelatine method No. 1 would be reported as containing 0.217 per cent. acetic acid and No. 2, 0.276 per cent., whereas, by vacuum distillation and phenolphthalein as an indicator, they are shown to contain only 0.0732 per cent. and 0.0876 per cent., respectively, of acid which may be calculated as free acetic. That the latter figure more nearly represent the actual free acetic contents is a reasonable conclusion, as we will show later.

It is obvious that the gallic and residual acids, which constitute over two-thirds of the total, are improperly reported as acetic and, if the acid value of a liquor means anything, they must be estimated for what they are. In No. 1, using phenolphthalein as an indicator, we find 0.335 per cent. gallic acid and in No. 2, 0.333 per cent., or approximately four times as much as the acetic found by distillation. As for the residual acids, we cannot express their value in terms other than in cubic centimeters of N/10 NaOH, as we do not know what they are. That they are all lactic or butyric is improbable for reasons which will follow.

Referring further to the foregoing analyses, the discrepancy in the figures given by hematein and phenolphthalein as indicators will be noted. This is apparently one of the weak points of hematein as an indicator. It being claimed that it gives good results on acetic acid, we thought the difference might be due to the impurity of the acids isolated from the liquors but, after a series of tests with C. P. acids, the following example is a fair illustration of the difference we found in results given by the two indicators, using N/10 NaOH to titrate with:—

	Phenolphthalein	Hematein
Acetic acid ($HC_2H_3O_2$)	10 cc.	8.44 cc.
Gallic acid ($C_7H_6O_5$)	10 cc.	8.00 cc.
Lactic acid ($H_2C_3H_4O_3$)	10 cc.	9.47 cc.
Sulphuric acid (H_2SO_4)	10 cc.	9.90 cc.

A further attempt to check these figures was made by titrating

Digitized by Google

mixtures of known volumes of these acids, the results being all lower with hematein than phenolphthalein, tends to confirm them.

In the case of acetic acid we find great difficulty in determining the exact end-point, as the reaction seems to be a double one, the second change on pure acid being faint and difficult to demark. In the case of determining acid in a yard liquor, this change is probably more distinct on account of the mixture of acids and the fact that some one of them is neutralized before the others, which, if true, suggests that hematein might possibly denote to some extent the proportions of a mixture of acids. With regard to the other three acids, the end-point is much more distinct. The resulting low figures, however, may be due to the color of the hematein being changed by the salts formed during the titration before complete neutralization.

If the analyses like Nos. 1 and 2 can be confirmed, the hematein-gelatine method, it would seem, not only fails to estimate the solvent and plumping value of the acids but does not give even a correct estimate of the total acidity.

To those who may be interested in following up this work a description of the methods employed to obtain the results given in analyses Nos. 1 and 2 may be useful. To determine the free volatile acid, 50 cc. of filtered liquor (specific gravity usually 1.012-1.020) was distilled in a porcelain and glass vacuum apparatus over a water-bath at a vacuum of about 26 inches to dryness, the distillate being condensed and caught in a double-necked flask. Then successive portions of 50 cc. of distilled water were added and distilled off, each time to dryness, until the distillate coming over was neutral. We find the first three portions usually take off 80 per cent. of the acid and that eight in most cases will reduce the distillate to neutrality. The distillate is then made up to volume and several aliquot portions titrated with N/10 NaOH and phenolphthalein and calculated as acetic acid.

We have every reason to believe that the free volatile acid is completely recovered without decomposition of the liquors, as numerous tests made of liquors proved that neutral distillates could be obtained even in the presence of sulphuric acid, and we

Digitized by Google

also find that a known volume of acetic acid added to a liquor containing no free volatile acid can be completely recovered.

To determine the gallic acid, the dry residue from the volatile distillation is dissolved in hot water and, after cooling, made up to its original volume. Twenty-five cc. are then pipetted into a dry 200 cc. stoppered flask or, better, to a separatory flask and shaken for five minutes with 100 cc. of absolute ether. The flask is then allowed to stand until complete separation of the ether and liquor has taken place, when the supernatant ether solution is decanted into a 1,000 cc. distilling flask or, when a separatory flask is used, the liquor is drawn off into a second similar flask and the ether into the distiiling flask. This procedure is repeated until a test made by evaporating 25 cc. of the ether shows no residue or, in case of one, no reaction for gallic acid when dissolved in distilled water and tested with a few drops of potassium cyanide solution.

The collected ether solution is distilled over a water-bath and the ether recovered. The residue, which contains water taken up by the ether, is then dried in the water oven to dryness and, when completely dry, the gallic acid dissolved out by repeated washing with hot water, made up to volume and titrated as in the case of the volatile acid and calculated as gallic acid. The portion of liquor from which the gallic acid has been removed is then gently boiled to remove the ether taken up during the shaking, then made up to the original volume and an acid determination made by the hematein-gelatine method, or any other preferred, to determine what we have termed the residual acid.

During our experiments we have frequently found that the ethereal residue was not completely soluble, even in hot water, an acid resinous substance remaining undissolved, which is readily soluble in weak alkali or 50 per cent. alcohol. Whether its presence is due to imperfect filtration or whether it is a resin held in solution by the acids in the liquor we have not determined. A 50 per cent. alcohol solution, however, gives no precipitation with gelatine, nor does it respond to the potassium cyanide test for gallic acid, though it gives a blue-black color with ferric alum.

In determining the gallic acid as described, the possibility of

Digitized by Google

including other acids soluble in ether must not be overlooked, that is, if they are presented to an appreciable extent. Tests made of the solubility in ether of the four acids discussed show acetic is only slightly soluble under 1 per cent. but is readily so in stronger solutions, but, as it can be removed before shaking out the gallic acid, it is not a factor. Lactic is quite soluble in all strengths, and here there may be some error, although, if much lactic acid were present, we do not think the dry crystalline residues from the ether solubles could be obtained. Sulphuric acid is only very slightly soluble, even in strong solutions, and it also may be ignored.

Doubting very much if the foregoing mode of procedure would lead to anything when applied to the more complex liquors of the yard, especially those of the handlers, a series of tests was made of the head and tail handler liquors, composed chiefly of hemlock, chestnut and quebracho, which we knew to contain sulphuric acid, the presence of which would predicate difficulty in recovering the free volatile acid without breaking up the acid forming constituents of the liquors into acid. We herewith give two examples of the results obtained:—

A—HEAD HANDLER LIQUOR.

Spec. Grav. 1.022. Expressed in cc's of N/10 NaOH.

Volatile acid	14.10 cc.
Gallic acid	12.40 cc.
Sulphuric acid (H_2SO_4)	75.00 cc.
Total	101.50 cc.

Total acidity by the gelatine-hematein method = 80 cc.

B—TAIL HANDLER LIQUOR.

Spec. Grav. 1.016. Expressed in cc's of N/10 NaOH.

Volatile acid	11.40 cc.
Gallic acid	8.00 cc.
Sulphuric acid (H_2SO_4)	76.00 cc.
Total	95.40 cc.

Total acidity by the gelatine-hematein method = 70 cc.

Reviewing these experiments, we found the volatile acid was as easily recovered and neutral distillates obtained as in the case of the fresh chestnut liquors, neither were any complications observed in shaking out the gallic acid, the ether soluble residue

Digitized by Google

showing no sign of sulphuric acid when dried for several hours at 100° C.

The determination of the free sulphuric acid, however, was somewhat of a problem, as we know of no very satisfactory method of doing so. To obtain the figures given in the test analyses, we proceeded as follows:—

A portion of the liquor was made strongly acid with acetic acid and an excess of barium chlorid added. The precipitate was then incinerated and the ash dissolved in HCl, and the H_2SO_4 determined in the usual gravimetric way.

Next a portion of the liquor was ashed and the combined H_2SO_4 calculated from the sulphates. The difference between the two results was taken as the free sulphuric acid. Here again the most striking thing is the discrepancy between the results for total acid given by the gelatine-hematein and the isolated acids.

Taking the analysis of the head handler liquor, we find that by the gelatine-hematein method the total acidity was equivalent to 80 cc. of N/10 NaOH, while the quantity required for neutralizing the isolated acids, without taking into account any fixed organic acids not estimated, totals 101.5 cc. Naturally this brought to mind the question of acid absorbed and carried down by the gelatine precipitate. When organic acids only are present, it is claimed this source of error is negligible but, remembering the greater activity of sulphuric acid upon gelatine compounds, a series of tests was run, which indicates the difference in question can probably be accounted for by the absorption of acid by the gelatine precipitate.

As a demonstration, a liquor known to contain acetic and gallic acids, but no sulphuric, was used. In one portion the total acidity was determined by the gelatine-hematein method. To a second portion 5 cc. N/10 H_2SO_4 was added and the total acid determined in the same manner as the first.

On titration, the first portion gave an acidity equivalent to 5.87 cc. N/10 NaOH and the second an equivalent of 8.91 cc. instead of the theoretical 10.87 cc., which shows a loss of about 40 per cent. of the added sulphuric acid. Repeated tests confirmed not only the foregoing but also a failure to obtain concordant results. We therefore believe the question raised should

Digitized by Google

be immediately investigated by others as, should this loss of acid be confirmed, the usefulness of the method will be still more restricted than it is now.

In order to simplify matters, we have only submitted a few results, which are typical, however, of those covering quite an extended series of experiments and, as previously stated, we do not claim anything for their accuracy. At the same time we believe they afford sufficient information to indicate the problem of acid determination will have to be attacked in a different way than has been done heretofore and also that no method will prove sufficient that does not differentiate and estimate, with a fair degree of accuracy, the constituent acids in liquors.

In the matter of acid determination, we are falling behind the English and Continental chemist, but it is unnecessary to refer to the work of Sand & Law and also that of Proctor and R. A. Seymour-Jones, as you are doubtless familiar with their recent papers.

In the past the importance of acid determination has been considered only in its application to tanning by the tanner and tannery chemist, but recent developments in extract making prove it is a matter of great importance to the extract maker. It is well known that all extract liquors and extracts contain considerable quantities of acids. This is especially true of chestnut wood extracts and, as the nature of these acids indicates they are secondary products, resulting from the decomposition of the extractive matter, it is of vast importance to the extract maker to be able not only to determine their character and quantity but also to follow them up through the various stages of manufacture. For instance, we know large quantities of acetic and gallic acids are found in chestnut wood liquors, part of which is formed during the growth and seasoning of the wood and part of which is formed during the processes of manufacture at the expense of the tannin and also of the most valuable acid-making non-tannin. Until these acids can be qualitatively and quantitatively determined throughout the various stages, it is impossible to intelligently attack the problem of modifying or preventing their occurrence.

If all the matter converted to acetic acid could be preserved in its original form and the gallic acid preserved as tannin, the

Digitized by Google

tanner would not only have a better tanning material, but the extract maker would effect a great economy.

Discussion.

Mr. Loveland remarked that the present method for acid determination gives results which do not show the plumping effect of which a liquor is capable for even if all the acid present is acetic, the presence of sugar or salts hinders the plumping action.

Mr. Reed, referring to Mr. Kerr's contention that we should have means of finding what acids are present in liquors, said that a first essential is to find out what is the effect on hide of each of the different acids in various proportions and mixtures.

Mr. Yocum remarked that it would appear that acid determinations by our present method are wasted time. Referring to Mr. Loveland's remarks, he called attention to the fact that the ionization theory explains why the presence of sugar or salts hinders the plumping action of an acid. The greater the concentration of a solution, the smaller the area in which a molecule of acid can work, its freedom of motion being less because of other substances present. Referring to Mr. Kerr's method, in which he distills to dryness, and after adding distilled water gets a further quantity of acetic acid, he suggested that this pointed to the conclusion that acetic acid is produced by dissociation of other substances present.

Mr. Kerr admitted such a possibility and said that a method should be found which will determine this point and others equally unsettled. He further said that if acetic acid be added to an extract containing 50 per cent. water and no acid, and the liquor distilled to dryness; distilled water added and the distillation repeated until a neutral distillate is obtained, the whole amount of volatile acid obtained will not exceed the acetic acid added.

In answer to further questions, Mr. Kerr said that the intent of the paper is to show that the present acid method is unsatisfactory, and to the extract maker useless. A method is needed that will differentiate the acids and estimate them with a fair degree of accuracy. Chestnut liquors contain more acid than has been supposed, and in some cases show a comparatively high acidity while containing no plumping acids whatever.

Digitized by Google

Mr. Yocum said that since chemical methods do not show the plumping effect of a liquor, an empirical method must be devised that will show it.

Mr. Kerr said that in the extraction of chestnut wood a considerable breaking up of both tannins and non-tannins occurs.

Mr. Yocum mentioned finding in a shipment of chestnut extract in barrels, several pounds of gallic acid in each barrel. The extract was therefore a supersaturated solution of gallic acid, and liquors made with such an extract would show acidity due to the gallic acid, while there might be no plumping acid present.

Mr. Reed asked for opinions from those who have had extensive experience with the gelatine-hematein method, whether it gives any information worth having.

Mr. Oberfell said he got little of value from the acid determinations.

Mr. Mosser said that the increase or decrease of acid in a given yard is sometimes an important indication, giving a check on how the yard is running, while acid tests on liquors from separate yards give very little basis for a comparison of the different yards.

Mr. Morrison said that in a yard where extract liquors are used, he is adding the acid necessary for plumping, and that although the quantity of acid added is uniform, the quantity found varies from day to day. He supposed the variation might be due to the varying weight of the hides. Mr. Smoot confirmed this suggestion, saying that heavier hides use up more acid than lighter ones.

THE TANNINS.[1]

By A. W. Hoppenstedt.

My object in addressing you to-day on the subject of the tannins, is to instigate a general discussion and to arouse your particular interest and individual effort in the problem of placing these substances within our power of discrimination.

There is no subject, to my mind, more interesting and fascinating to the leather chemist than the experimental work under-

[1] Paper read at the A. L. C. A. Convention, Washington, D. C., December 9, 1911.

Digitized by Google

taken for the purpose of finding suitable ways and means for identifying and detecting the different tannins. It may seem to many that only those chemists can undertake such work who have a great deal of time to spare, but though this may be true to a large extent, nevertheless most leather chemists have a little available time now and then which can be utilized for research purposes and which will, in the long run, by patience and perseverance, yield valuable achievements. We have no institutions in this country like those in Europe, where scientific researches in problems of the leather industry are constantly being conducted, and as our conditions here are very different from those abroad, it is up to us, to the individual chemist, each doing his share, to advance our knowledge and increase our usefulness, which the changing times demand.

It seems to me that it is equally the duty of the tanners of this country to urge their chemists to effort along these lines, and it is rather surprising to note, considering the importance of our leather industry and America's well-known enterprising spirit, that the tanners of this country, the individual tanners as well as the tanning corporations, do not employ, to my knowledge, a single chemist for research purposes.

As you all have probably seen from our JOURNAL, I have commenced the long and arduous task of investigating and defining all reactions published for the detection of the different tannins, combined with an endeavor to establish additional ones, especially for those tannins which we have no means of distinguishing. I am sorry that I have been obliged, owing to lack of time and some materials, to allow considerable time to elapse between the installments of my current article. However I realized at the commencement that the work was one which would require a long time to complete, especially when considering that it is necessary to keep from ten to twenty different tannin solutions under observation at the same time and which must be repeatedly freshly prepared.

In my opinion, the lines offering the greatest possibilities for success, are those dealing with the solubility of the tannin compounds, and I have become convinced that any search for distinctive color tests alone, will never lead very far.

Digitized by Google

I should like to note here that experiments practically indentical with those made by E. Stiasny and C. D. Wilkinson, (*Collegium,* 1911, 475, 318) on the solubility of the lead salts of the tannins in acetic acid, were made by me some time before their work was published, and the results I obtained agreed very closely with theirs, but I discarded them as being of no value for the identification and detection of any tannin. While speaking of the lead salts, I should like to point out, though probably many of you have noticed it, that the filtrates of some tannin solutions when precipitated with normal lead acetate instead of the basic lead acetate, are strongly colored. This is due entirely to the greater solubility of the lead salts of the catechol tannins in acetic acid, and you may recall that I protested at our last annual meeting, against the adoption of the normal lead acetate in place of the basic lead acetate for precipitating the tannin in the determination of the glucose.

An interesting line of experiments with which I have been occupied for some time, and which have yielded results of value, consist of solubility tests of the compounds of the tannins with the alkaloids. I have observed some very marked differences in the solubility between these compounds of the different tannins in various reagents, and I have been chiefly studying the solubility in acids of the tannates of quinine, cinchonine, strychnine and atropine. Of the tannates of cinchonine, the most insoluble one in the presence of acetic acid, is chestnut, while in the presence of sulphuric acid, quebracho is most insoluble.

A further line of experiments which I have under observation, are solubility tests of the precipitates formed by gelatine, in various mediums. An interesting feature noted here and one not previously known to me, though possibly many of you are aware of it, is that in the presence of considerable acetone, gelatine solution does not precipitate tannin.

The field of solubility experiments is a very extensive and interesting one; and one which affords ample opportunity to the persistent worker to achieve results of much value. In the forthcoming installments of my current article, I shall publish two new tests, based on the solubility, which I have established

Digitized by Google

for the identification and detection of the tannins of hemlock and mangrove.

In closing, I wish to again urge upon you the desirability of giving some of your attention to work along these lines, for it is necessary to find suitable tests for quite a number of the tannins. I am sure I would be most willing and glad to render to any of you who are ready to take a hand, all the assistance and coöperation I can.

Discussion.

Mr. Veitch:—Mr. Hoppenstedt has tackled a very important and difficult problem, in which he has my sincere sympathy. If any of you can give him any help or suggestions I know he will be glad to have them. It is an exceedingly important line of work. Is there any discussion on the subject?

Mr. Claflin:—I would like to ask Mr. Hoppenstedt if he has done anything in regard to the optical activity of any of the salts of the tannins. I should think there was a possibility of some of their salts showing optical activity. In that way you could get a means of separation that was really easier to apply than the solubility of the salts, because I know from work on the various fatty acids that the solubilities of the different salts is a very difficult thing to apply and to get concordant results in the case of mixtures.

Mr. Hoppenstedt:—In the case of mixtures of tanning materials I find the best way to proceed in solubility experiments is to endeavor to find substances which will remove all or nearly all the tannins from the solution except the one sought after, which latter remains because of its greater solubility. In regard to the optical activity of the salts, it seems to me that that would be a very interesting line to pursue. I would like to ask Mr. Claflin if he means optical activity of the tannins with the alkaloids, or whether he means any compounds of tannins?

Mr. Claflin:—It would undoubtedly be organic compounds.

Mr. Hoppenstedt:—All the alkaloid salts of the tannins would be optically active. Most of the compounds of the tannins would be of such a dark color that there probably would be considerable difficulty in examining them in a polariscope. That is the one objection that I see to it.

Digitized by Google

MR. SMALL:—Are these compounds of the alkaloids soluble or insoluble?

MR. HOPPENSTEDT:—In neutral solution they are practically insoluble.

MR. VEITCH:—If Mr. Hoppenstedt has a method by which he can precipitate all the tannins except the one he wants, I think he has made a big step forward.

MR. GRIFFITH:—With regard to Mr. Hoppenstedt's statement on the precipitation of gelatine, I understand Mr. Hoppenstedt to say that under chemically pure conditions this precipitation does not take place. I first saw that statement made by Wood some time ago, and I would like to ask Mr. Hoppenstedt whether in corroborating that statement he would attribute the precipitation when it does occur to physical rather than chemical conditions.

MR. HOPPENSTEDT:—It seems to me that it must be due more to physical than chemical conditions.

DISCUSSION OF COMMITTEE REPORT ON LEATHER ANALYSIS.[1]

Mr. Veitch reviewed the report published in the December JOURNAL, and called attention to some errors in the published account. (See p. 132, this issue.) We print the discussion which followed, partly verbatim and partly in abstract.

MR. FAUST:—I think the recommendation in regard to the determination of fats will put that matter on a good basis. I believe the time of extraction for leathers containing up to eight or ten per cent. grease, should be placed at about six hours. I am pretty sure that the work of the committee shows that that is sufficient; and for harness leather I believe that ten hours is sufficient.

In reference to the work done on the glucose, I think the method that Mr. Veitch sent out for the committee to work on is preferable to the present method, especially the use of potassium oxalate for removal of the lead. I want to ask whether a large excess of potassium oxalate had any direct result on the percentages found.

[1] Washington Convention, A. L. C. A., Dec. 8, 1911.

Digitized by Google

MR. J. S. ROGERS:—I haven't notice that a reasonable excess of potassium oxalate made any appreciable difference. The method that I usually follow is to add a sufficient excess of potassium oxalate so that I am sure that all of the lead or practically all of the lead is precipitated. Of course if there is a small amount of lead left it is taken out by the sodium carbonate on the final neutralization, and filtration removes it. So that no difficulty is caused from that. It has been my experience that a reasonable excess of potassium oxalate doesn't make any difference.

MR. OBERFELL:—I would like to ask Mr. Veitch if it makes any difference as to the volume of the solution when inverting sugar.

MR. VEITCH:—I don't see that it would make any appreciable difference.

MR. OBERFELL:—It is my recollection we had some discussion on that a year or two ago and you recommended that 90 cc. was the proper amount to invert.

MR. VEITCH:—As I remember that, it was a question of concentrating the solution. This proposed method provides that there shall be no concentrating of the solution. That is the important point because by concentrating, sugars are destroyed.

MR. OBERFELL:—Then the volume would make no difference?

MR. VEITCH:—Absolutely no difference, provided you do not concentrate at all in the boiling.

MR. MOSSER:—I would like to ask Mr. Veitch if he made any nitrogen determination on water soluble.

MR. VEITCH:—Yes. I might have mentioned that. I think not in connection with these leathers, but on a dozen other samples we have run them, for weeks at a time. The same leather was extracted continuously, in periods of two days each for several weeks, and we found no nitrogen coming out at the end,—none whatever.

MR. SMALL:—That is no nitrogen at all throughout the whole process?

MR. VEITCH:—At the beginning there would be a trace. It was so small that we never calculated the figures to percentage.

Digitized by Google

MR. DELANEY:—The method for determining sugar says to take 5 cc. of concentrated HCl and boil it with the reflux condenser for two hours. I had thought that the Department of Agriculture method was to take the same quantity of muriatic acid and heat at 68° C. for not over ten minutes, owing to the fact that the tannin is liable to be converted into glucosides.

MR. ROGERS:—When the sugar is determined the tannin has been removed by lead acetate, so there will be no tannin present.

MR. ALSOP:—Have you tried determining the sugar in solutions of certain tanning materials with normal lead acetate? I mean solutions that contain only quebracho, for instance, or only hemlock.

MR. VEITCH:—We have not. We have not had an opportunity, so far, to do so.

There is another thing that I think might be done. Ordinarily, I believe there is very little gained by boiling with hydrochloric acid at all, and perhaps the difference with and without hydrochloric acid would be so small that it is hardly worth while going through this procedure. Of course in those materials that contain starches it would make some difference.

MR. SMALL:—In the case of extracts where you are estimating the amount of sugar in the extracts themselves it certainly makes a marked difference whether they are inverted or not.

MR. VEITCH:—That inversion is made without removing the tannin?

MR. SMALL:—No; after removing tannin with lead acetate.

At this point a question was raised in regard to the material which is extracted from leather by water at 50° but settles out in cooling. Suggestions were asked for in regard to how this residue should be reported. Mr. J. S. Rogers said that except in the case of undertanned leathers the residue was negligibly small. Mr. Small suggested that the deposit might be due to the combination of extracted gelatine with tannin in the solution, and asked whether a Kjeldahl determination showed more nitrogen in those water extracts than in others. Mr. Rogers had no data to offer. Mr. Veitch expressed the opinion that the amount of nitrogen in the residue was in any case very small. Mr. Reed had done some work on book binding leathers which were rather

Digitized by Google

lightly tanned, and had found a larger amount of sediment from the water extract than usual. He had not determined the nitrogen in it. Mr. Veitch suggested that some work ought to be done on this matter.

MR. J. S. ROGERS:—I would like to ask if leather in being extracted with water is decomposed or distintegrated, will the nitrogen remain with the residue or will it come out in the extract? If we do not get nitrogen in the extract is it an indication that the leather is not broken up? I refer to the presence of nitrogen in the extract, due to long extraction, not to use of excessive temperature.

MR. CLAFLIN:—I think there must be some dissociation of the leather because we all know that in higher temperatures the hide substance and tannin are dissociated, and from all scientific reasoning, the difference in temperature should simply cause a difference in degree of dissociation and just because it gives, you might say, results that are so below the limit of error, you cannot say there is not some decomposition of the leather. I think we should recognize the fact that the leather, the tanned hide substance, is not an absolutely insoluble composition in water, and I do not think the fact that we do not find it in the residue is a proof none remains behind in the leather. I think you approach an undertanned leather after you have washed out the excessive tannin.

MR. VEITCH:—I think there is no doubt whatever that leather is broken up by washing with water, and it is only a question of degree. The hotter the water, the earlier it begins to break up; but the point that I have in mind is that this does not occur as early in extraction as we might be led to believe. For instance in the work where we ran extractions for weeks, when the soluble matter removed by 14 hour's extraction was down around 0.3 per cent., we had reached a constant rate of solution, and you get down to that point where you are undoubtedly dissociating the leather substance itself at a very, very slow rate.

MR. OBERFELL:—In obtaining this water soluble material I have found that the tannin which is most soluble is that which comes over first. The difficulty is in knowing, so to speak, an end point, where we get no tannin or other soluble matter. Our

Digitized by Google

method calls for the digestion of the leather with water at 50°, and then the extraction. The material which is most soluble is that which we get out first, and I have found it is an advantage in the extraction to start immediately and allow the most difficultly soluble material to be soaked over night, that is at the end of the extraction rather than at the beginning. I get a clearer solution that way than by soaking it at the beginning of the extraction.

MR. HOPPENSTEDT:—Do you obtain colorless filtrates after precipitating tannin solutions with normal lead acetate?

MR. J. S. ROGERS:—The filtrates are practically colorless; in some cases they have a very slight yellow color, but do not give an appreciable reaction with gelatine salt solution.

MR. HOPPENSTEDT:—The lead salts of the catechol tans are rather soluble in acetic acid, whereas the lead salts of the pyrogallol tans are not. In precipitating a catechol tannin with the normal lead acetate the soluble lead salts of the catechol tan go into solution, and naturally you would not get any reaction with gelatine salt solution. I have found, working with the catechol tannins, as stated, that they are rather soluble and you get a considerable amount of them in the filtrate, which you do not get when using the basic lead acetate. It seems to me when you precipitate with the normal lead acetate and then remove the lead, you have tannin in the free form in the filtrate. That tannin will then act on the Fehling solution. We all know that basic lead acetate removes a small amount of glucose or sugar, but I am of the opinion that by using the normal lead acetate we introduce a greater error by leaving tannin in the solution than we do by removing a small amount of the glucose with the basic lead acetate. The results of the committee seem to show that using normal lead acetate, the correct amount of glucose was found, that is, the amount that was put in plus the amount that was present, whereas using the basic lead acetate it was considerably lower. The difference between the basic lead acetate and the normal lead acetate was about one and one-half per cent. in the leather containing about eight per cent. of sugar it was about half that amount. It seems to me that ratio does not seem quite in proportion. Have you thought of that, Mr. Veitch?

Digitized by Google

MR. VEITCH:—I did not know of any reason why there should be a proportional ratio. You will understand of course, that errors of two- or three-tenths are to be expected, so when you come to figure ratios on two samples only, it is rather a risky matter.

MR. HOPPENSTEDT:—Well, I was simply taking the average in the results. I just wanted to bring that out, that is all. It seems that with 8 per cent. of sugar, the difference was 1½, whereas when it was only 2 per cent. of sugar the difference was 0.8. Will you let us hear what you think of the tannins remaining in the filtrate?

MR. VEITCH:—Well, I will say this, that it sounds very plausible, and it may be true, but it does not agree with the facts that we now have in our possession. I think we have had some hemlock leathers that have had glucose added to them and have still gotten the same kind of results, that is we have not been able to get the sugar that we knew was there with the basic salt, and we have gotten approximately what we knew was there with the normal salt. Now I think the point you have made, and it was made by Mr. Blockey, also, possibly needs some further study, but as I say, on a sumac tanned leather where you certainly have the condition of which Mr. Blockey speaks (the presence of gallic acid) we have gotten better results by the normal than by the basic lead acetate.

MR. HOPPENSTEDT:—I do not know just what the solubility of gallic acid is. I think the trouble would be more with the catechol tannins. The two leathers you had were oak tanned leathers.

MR. VEITCH:—Yes,—said to be; whatever that means to-day.

MR. HOPPENSTEDT:—Now chestnut is about the most insoluble of all of the lead salts, and oak follows pretty close to chestnut; it acts much like a pyrogallol tannin when precipitating with lead; more than it does like a catechol.

MR. VEITCH:—Is it not pretty well acknowledged that oak bark tannin is a mixture of the two?

MR. HOPPENSTEDT:—Yes, but the catechol tannin predominates in oak.

Digitized by Google

MR. VEITCH:—Well, I feel safer then about the accuracy of the results if that is so.

MR. HOPPENSTEDT:—Oak, though a catechol tan, acts with lead more like a pyrogallol tannin; that is the point I was bringing out.

MR. VEITCH:—Your point would be that a quebracho or other catechol tannin would behave differently from oak?

MR. HOPPENSTEDT:—Decidedly.

MR. VEITCH:—Although the oak is a catechol tannin?

MR. HOPPENSTEDT:—Yes. The lead salts of quebracho are very soluble.

MR. VEITCH:—I do not recall definitely that we have worked with the hemlock leather to which we have added a known amount of glucose. We have worked on the matter for several years, but I do not recall that definitely, though I think we have.

MR. HOPPENSTEDT:—In a work published by Stiasny and C. D. Wilkinson awhile ago, in determining the solubility of lead salts, they found the same as I have found, that the catechol tans were all very soluble and the pyrogallol tans were not, and they recommended that as a means of detecting some pyrogallol tannins.

MR. REED:—I have not gone into the matter at all deeply the way Mr. Hoppenstedt has, but I have had trouble with getting quite highly colored filtrates using normal lead acetate. I do not know what to attribute it to.

MR. VEITCH:—We have had trouble even with the basic. I think that is more a question of procedure than it is the salt used.

MR. J. S. ROGERS:—I have found that in the filtration if you are not careful to return the filtrate several times with the normal lead acetate you get a sort of color which in reality is a sort of gelatinous precipitate. That often is so; whereas if you return the solution to the filter you get a practically colorless filtrate.

As regards the proportion of difference on those two samples of leather, I would like to ask if the basic lead acetate removes sugar, how does it remove it? Is it occluded in the precipitate? If that is the case would not the proportion of sugar removed by the use of basic lead acetate be in proportion

Digitized by Google

to the volume of the precipitate? And if the volume of the precipitate varied would not that explain the variation in the proportion of sugar removed in different cases?

MR. HOPPENSTEDT:—I do not think it would. I think the action that takes place there is the formation of lead glucoside.

MR. ALSOP:—Our old method used to say to take 500 cc. of the extractive solution and precipitate with 20 cc. of the lead acetate. In my experience 20 cc. was generally sufficient; but the new method says to take 200 cc. and use 25 cc. of normal lead acetate. Do you think that would make any difference in results?

MR. VEITCH:—We found the other quantity too small, I think. We had to increase the proportion of lead used.

MR. ALSOP:—It is a pretty large increase.

MR. VEITCH:—It is.

MR. ALSOP:—I have used the other for a number of years.

MR. HOPPENSTEDT:—I would like to ask Mr. Veitch if he has made any determination of the sugar in extracts by means of normal lead acetate?

MR. VEITCH:—We have not worked on extracts at all.

MR. ALSOP:—I would suggest that the association have some work done on the determination of sugar in tanning extracts containing only one tanning material, with the normal and basic lead acetate, to see what results could be gotten. I know in precipitating hemlock for instance I cannot get a colorless solution with normal lead acetate. I have not carried the work far enough to know what the results will be, but I cannot get a colorless solution, when I can with the basic lead acetate. I think it would be a good thing to have some work done on it.

MR. YOCUM:—I would like to call attention to the fact that Mr. Hoppenstedt has brought out. If there is going to be any work done on sugar content of leather extracts, both pyrogallol and catechol tannins should be worked on, because the analysis of a chestnut extract with the normal lead acetate as a precipitant would be rather different from what it would be in the case of a pure catechol such, for instance, as hemlock extract, and it would be useless to base a presumption on the use of one extract or material, if it happened that it was pyrogallol or catechol as the case might be.

Digitized by Google

MR. FAUST:—I would like to know what objection Mr. Alsop has to such an increase in the amount of lead acetate used. Do you object on the theory that it would influence the result?

MR. ALSOP:—I only asked the question whether it would give a different result.

MR. VEITCH:—It has been our experience that the other quantity proved too small with the normal lead acetate, and, as you truly say, this is a large increase and it seemed large to us, but we made it on the safe side.

MR. FAUST:—That has been my experience. In using 500 cc. of the extractive solution and only 20 cc. I repeatedly got colored filtrates, but when using the quantities we are talking about now I have not had a colored filtrate,—although I have not had a hemlock tannin.

MR. VEITCH:—You certainly had quebracho tanned leather.

MR. FAUST:—Not completely tanned with quebracho. I have worked on several samples containing mixtures, but I have not worked on any pure catechol.

MR. VEITCH:—As I understand you, you stated here, Mr. Hoppenstedt, that oak tanned leather behaved like a pyrogallol tannin. Did I understand you correctly?

MR. HOPPENSTEDT:—I said that particularly of oak.

MR. VEITCH:—But you say it would not hold in another combination?

MR. HOPPENSTEDT:—I say if you have a mixture of a pyrogallol and a catechol.

MR. VEITCH:—Which you have in an oak.

MR. HOPPENSTEDT:—Take for instance quebracho and chestnut. The lead salts of chestnut are very insoluble, but of quebracho are very soluble. If you precipitate a mixture with the normal lead acetate you will get lead salts of catechol tannin in the filtrate. The chestnut will not carry down the catechol tannin. I have done a good deal of work on that and I know that to be the case.

MR. VEITCH:—You think the oak will carry down?

MR. HOPPENSTEDT:—More or less, yes.

MR. ALLEN ROGER:—I would like to ask if in the methods of this association as they are now carried out there are 20 or 25

Digitized by Google

cc. of normal lead acetate added to 500 cc. of extract? Is that the way it is carried out at present?

MR. VEITCH:—That is the way it is laid down.

MR. ALLEN ROGERS:—If that is the case, then I am not surprised that you get colored filtrates, because you ought to have a larger proportion of normal lead acetate to the extract. I think that explains perhaps why you get colored filtrates in certain cases.

MR. YOCUM:—If Mr. Hoppenstedt's statement is correct, that the lead salts of the catechol tannin are soluble, then the quantity of lead acetate added will make no odds. It is simply a question of the solubility of the lead salts.

MR. HOPPENSTEDT:—That is all.

MR. VEITCH:—Is not the lead salt less soluble in an excess of the lead acetate?

MR. HOPPENSTEDT:—That I do not know.

MR. VEITCH:—That is true as a rule, you know; that is, barium sulphate is less soluble in an excess of sulphuric acid or barium chloride than it is in water.

MR. HOPPENSTEDT:—That may be so.

MR. VEITCH:—And it is possible that this large excess of the normal salt of which Mr. Alsop has spoken, has something to do with ensuring a more nearly colorless filtrate and less of the catchol tannins going through.

MR. HOPPENSTEDT:—Yes, I think that is right.

MR. VEITCH:—That may possibly account for the apparent differences that two sets of workmen are getting.

MR. HOPPENSTEDT:—Yes, because I have found that with some filtrates of catechol tannins, after precipitating with normal lead acetate and adding a small quantity of salt, that the precipitate will go down; you will get a colorless filtrate.

MR. VEITCH:—Mr. Rogers spoke of the importance of returning several times and pointed out that that so-called colored solution was often a colloidal precipitate running through. That is also additional evidence along the same line.

MR. J. S. ROGERS:—Does not the presence of a large excess of the neutral lead acetate tend to render this precipitate, if it is soluble, less soluble? Would it not have that tendency?

Digitized by Google

MR. HOPPENSTEDT:—That is just what we are talking about.

MR. J. S. ROGERS:—It seems to me that is the case. Another point I would like to ask is, supposing that there are some tannins left in the solution, is that error anywhere near comparable to the error that there is by using the basic lead acetate? We have analyzed some solutions that had practically no sugar in, using both the basic and the neutral lead acetate, and we have found practically no difference by the two methods. That is, where they contained say 0.3, 0.6 or 0.8 per cent. Now if in those solutions the normal lead acetate gave too high results why would it not show there? It does not.

When the method for glucose was revised the last time and neutral lead acetate was substituted for the basic acetate, the 500 cc. of solution used should have changed to 200 cc. of solution. This is the proper proportion. This error in the method as printed I think explains why so many chemists had trouble and got colored filtrates after precipitation with neutral lead acetate.

MR. YOCUM:—I think this can be said about the chemists who are operating the method, that we prefer the normal salt because of its greater ease and convenience of operation, and also that the normal salt would give more uniformity of results, enabling us to get better duplicates than with the basic. Mr. Faust has had some experience with that and I think he will agree with me.

MR. FAUST:—The committee of which Mr. Veitch is chairman might do a little work on the idea suggested by Mr. Alsop, that is to try the different catechol and pyrogallol tannins, and see whether there are any soluble lead salts in the filtrate from catechol tannins, and also see what effect it would have. I am willing to coöperate with Mr. Veitch if he would like me to do so.

MR. VEITCH:—If that work should be assigned to this committee and I should have anything to do with it, I should be glad to coöperate. I think I shall carry it on whether or not I have anything to do with the committee.

MR. REED:—Mr. Veitch, in the preparation of the samples for the leather analysis do you think anything should be done there to make it more specific in any way? It seems to me it

Digitized by Google

would make a considerable difference in the water soluble and fat and everything else.

MR. VEITCH:—I fully agree with you, and I do not know anybody who is better prepared to tell us about the preparation of leather samples than Mr. Small. I saw in his laboratory once a machine that I thought would do much better work than any I have seen elsewhere, better than I have myself. Our samples had some hard lumps in them, and it undoubtedly prolongs the extraction if it does nothing else. I have never been able to get one made, but I believe Mr. Small has a machine that will prepare a suitable sample of leather.

MR. SMALL:—The idea is not original with me. I think, as I have it in mind, I got the idea from Mr. Alsop originally. It is simply a collection of ordinary circular saws. In my particular piece of apparatus I have three saws side by side and a sliding table that feeds the leather up to the saws, and by regulating the feed of the leather you are able to regulate somewhat the fineness of the division; but it gives certainly a most excellent preparation of the leather and the most rapid of any that I know of. Simply a chewing of the leather up by means of these circular saws. My machine has a wooden frame. If any of you are thinking of building one I would not advocate a wooden frame, because the shrinkage and swelling with the weather makes the sliding of the feed apparatus extremely irregular and uncertain; but it is very easily made with a metal frame, in which case difficulties of that sort are obviated. If it is of sufficient general interest I should be glad to have the machine photographed and the prints put in the JOURNAL.

DISCUSSION OF REPORT OF COMMITTEE ON OILS AND FATS.[1]

After Mr. Oberfell's review of his report, published in the JOURNAL for December, 1911, the following discussion took place.

MR. HOPPENSTEDT:—I would like to ask Mr. Oberfell how he finds the viscosity compares with the emulsification; does there seem to be a relationship between them?

[1] Washington Convention, A. L. C. A., Dec. 7, 1911.

Digitized by Google

MR. OBERFELL:—I doubt very much if there is any definite relation between the emulsification and viscosity, although I think that really the value of a mineral oil depends on three principal points,—the gravity, the viscosity and the emulsification. If an oil has a proper relation between the gravity and the viscosity, I think that has a bearing upon the emulsification, but the emulsification test has been so unsatisfactory that it is very difficult to say what the relation is, if any.

MR. HOPPENSTEDT:—I did not mean so much from the committee work, but from your general experience.

MR. OBERFELL:—I think the emulsification depends largely on the treatment the oil receives at the hands of the refiner.

MR. SMALL:—May not the different results that were obtained by your emulsification test be due to the differences in the shaking for the production of the emulsification?

MR. OBERFELL:—Undoubtedly I think that has something to do with it.

MR. SMALL:—That seems to me a very probable explanation of the different results here. Have you ever tried a Dover egg-beater?

MR. OBERFELL:—No. That may be a very valuable suggestion. I think we would have to reduce it to some mere mechanical condition. It took longer for the emulsion to break for me than it did for the rest of the members, but I gave it a pretty severe shaking. Of course the size of the globules in the emulsion would depend largely on the rate of agitation. I would not be surprised if temperature had some influence on it too. If we could work up a good emulsification test and settle on some standard viscosimeter, we could get pretty concordant results on oil. I do not know about the evaporation test; I have no way of deciding whether it is temperature or the depth of the film of oil which is exposed to the heating surface or the length of time it is heated. I know this though; the most satisfactory oil is an oil which has a very low evaporation, and that it does not make much difference how accurate your results are, if the evaporation is high the oil is not good; but this is very unsatisfactory if two chemists are expected to agree on a report. Now the oil "B" which I sent out is an oil which is known to work

Digitized by Google

very satisfactorily for sole and belting leather. The loss by evaporation was low; the highest results, I guess, were under one-half per cent., and that was a very drastic heating; and some were under one-tenth per cent., showing that an oil which is really satisfactory is of very low evaporation.

I would like to have anybody who has had any experience with evaporation tests on oils tell something about it.

MR. FAUST:—I tried the evaporation test several times by weighing out about 0.2 gram of oil on a small piece of filter-paper. I laid the filter-paper on a watch crystal and dried it for four hours in a regular drier at about 98°. I always obtained fairly concordant results.

MR. OBERFELL:—Dr. Gill in his "Oil Analysis" gives a method similar to that. He gives directions for cutting out an annular piece of filter-paper and drying on that, giving a uniform surface for exposure. I found that it requires a great deal of time to get the paper properly desiccated and weighed. There is the difficulty; you are dealing with a very small quantity of the oil. The paper is dried and it has to be exposed in the balance while weighing out the oil. That was the reason I did not send this method to the committee to try out. I tried it myself and found that the paper absorbed moisture very fast on the balance pan.

MR. SMALL:—Weigh it in a stoppered bottle.

MR. OBERFELL:—The paper has to be weighed before and after evaporation. Do you weigh the paper in a stoppered bottle? It would not be a very convenient thing to dry it in, it seems to me.

MR. SMALL:—It works all right.

MR. OBERFELL:—That might be a very good suggestion. I do not know whether the paper would gain enough in weight to make any difference while the stopper was out of the bottle. I know that it does in an open crystallizing dish.

MR. REED:—Have you drawn any conclusion as to the emulsification of an oil so far as its acidity or alkalinity goes?

MR. OBERFELL:—No, because I have never had an oil that had any kind of emulsification that was not practically a neutral oil. There does not seem to be much difficulty about that. Most of the refiners seem to have their oil in pretty good shape in that respect.

Digitized by Google

MR. REED:—You found none that was slightly alkaline?

MR. OBERFELL:—No; but I have no doubt that would have considerable influence on it. I think the analyst would have to take that into consideration in his report.

MR. AGNEW:—I may help you out a little on the emulsification. Petroleum oils will not saponify, we know that, and petroleum products can only be treated up to a point of slight emulsification: that is, if you use the straight goods. It can go so far that when oiling an emulsion can be rubbed up (by hand or wheel oiling) to keep the oil from dripping. As regards viscosity, we can take an oil of a stated viscosity and treat so it will emulsify; it will not affect the viscosity. The point you bring the oil up to is its value as regards viscosity. The emulsification,—you can only get that so that in oiling in the wheel it will start up a certain emulsification to stop the drip. That is about as far as you can go with a petroleum product. For any greater emulsification you would have to compound with some other emulsifying oil.

MR. OBERFELL:—You do not think there is any relation between the body of an oil and the emulsification?

MR. AGNEW:—After it is refined and treated. You can take any oil and treat it for emulsification, and you would have to do something to it. You bring it up in the still to a certain point, to a certain viscosity, to a certain flash point, and then treat it for, we will say leather. After it is refined I think emulsification does not affect the viscosity; it would have practically the same viscosity, only the oil that is not treated for emulsification would drip from the leather while an oil which will emulsify will make a creamy protection for the grain and also keep it from dripping. Some oils treated for emulsification would smear the leather; another oil treated that way would penetrate the leather. Much depends on the crude oil used and the way it is refined.

MR. TEAS:—What Mr. Agnew says shows that in a straight mineral oil there is no relation between viscosity and emulsification.

MR. OBERFELL:—I have had the question of the ash brought up twice. Mr. Alsop said something to me once about it, as to

Digitized by Google

whether I found the ash of any value in deciding on the merits of an oil. I do not think so in a straight mineral oil. The ash can be practically ignored on a straight mineral oil, so far as my experience is concerned, but if it is an oil which is a mixture of any kind at all and the ash comes up, that would be another question for the chemist to decide from his examination. I do not see how the ash would apply to a straight mineral oil.

MR. REED:—Might it not apply if there was a certain amount of alkali left in the oil?

MR. OBERFELL:—There might be ash. Have you ever found ash to amount to anything in a straight mineral oil, Mr. Alsop?

MR. ALSOP:—Not in a straight mineral oil, but I have found the determination valuable in some that were not straight mineral oils. .

MR. OBERFELL:—Yes, a compounded oil. I believe that chemists can get a great deal out of the discussion of various kinds of oils. One of the principal points where there is difference of opinion is as to the relative value of the heavier or asphalt oils as against the paraffine oils,—Texas oils and Pennsylvania oils and so on. If there is anybody here who has had experience both in the laboratory and the tannery with those two kinds of oils I think it would be of great value to everybody to have the result of their experience.

MR. LOVELAND:—Do you mean the gain in the weight in using a higher specific gravity?

MR. OBERFELL:—That goes without any argument at all; but as to the relative effect the two oils have on leather,—Texas oil and Pennsylvania oil, to take those as two samples.

MR. LOVELAND:—One having a greasy base and the other asphaltic? Suppose a tanner should take, as they do, 1,500 pounds of leather to an oil wheel. That, on a loft basis, would mean about 750 to 800 pounds of actual loft leather. Now on a day's run, say he was wheeling with three gallons of oil to a wheel, to 1500 pounds of wet leather, would that have any direct bearing on the weight, providing the other oil was the better oil for the leather? The amount of oil used to a day's run is so small on the amount of the loft leather that the gain in weight of the

Digitized by Google

added specific gravity would make very little difference to the tanner.

MR. OBERFELL:—That may be. If you take a whole tank car and you figure it on that basis, why you can see considerable money in it; but if you figured on just how much it meant on a day's run, why it might not appeal to you so very much. I would like to know the character or the quality of the leather that the two oils make, as to the effect on the grain and the lubrication of the fibres and so on. You can tell the difference in the feel of the leather between the two oils.

MR. LOVELAND:—That was what I wanted to bring out, if an oil was doing good work in the tannery, even if it has a little less specific gravity than the other, if it worked well in the leather the weight would have no bearing on the subject.

MR. OBERFELL:—You known some oils give a leather that feels harsh.

MR. LOVELAND:—It does not give a cheesy cut to the leather.

MR. OBERFELL:—No, and experience in those things I think is what is going to help the chemist rather than a plain discussion as to how to analyze the oils.

MR. HOPPENSTEDT:—I do not think you can lay down a hard and fast rule for the treatment of the two oils, Texas and Pennsylvania.

MR. OBERFELL:—Then you think if a Texas oil was properly treated it would be just as good as Pennsylvania?

MR. HOPPENSTEDT:—I would surmise so.

MR. OBERFELL:—You see, the Texas oils are red oils and the Pennsylvania are amber. Some think that would naturally cause a darker color in your leather. I would like to know if anybody has had experience as to exactly what the result would be.

MR. AGNEW:—Gravity has very little to do in determining the value of an oil, excepting when comparing oils made from the same crude. Take say a high class filtered cylinder oil made of Pennsylvania crude, would weigh about 26 in gravity and the flash point would be about 575° F. or over. An oil made of Texas crude of say 21 gravity, would flash at 350° F., or less. It would weigh heavier than the cylinder oil by five points in gravity (about one-quarter pound per gallon) yet the cylinder oil would

Digitized by Google

be many, many points superior in actual grease value. In other words, oils properly refined from Pennsylvania crudes do not weigh quite as much as oils refined from an asphalt or tar base, but are much richer in grease value and take the place of animal or fish oils better for oiling any kind of fiber. Oils made from Texas crudes are mostly dark in color, but can be made light colored. In every case, my experience has been that the grain of sole leather oiled with Texas oils is not so clear and of as good color as leather oiled from an oil made from Pennsylvania crude. Texas crude sells at about 50 cents per barrel, while Pennsylvania crude sells at $1.30 and over a barrel. If the products of Texas oils were as valuable as the products of Pennsylvania, they would command the same price.

MR. OBERFELL:—How about the penetration of Texas oils?

MR. AGNEW:—Why, I do not believe they are as good.

MR. HOPPENSTEDT:—Emulsification?

MR. AGNEW:—Well, that depends on the way they are treated after being refined. Some oils are made to repel moisture; others are made to absorb moisture. That is because they want it for a certain purpose. For instance, take an automobile oil, an engine oil,—well let us say take the Erie engines. Now the oil is put in the crank case and the engine runs in oil. Any little moisture in there will make a very thick emulsion, if treated to emulsify. Oils for that purpose are made to repel moisture, so that is an entirely different condition from the requirements for oiling leather.

MR. OBERFELL:—How about the Texas oils; do they naturally repel moisture?

MR. AGNEW:—All mineral oils repel moisture to start with. Then you can make them as you want them.

MR. OBERFELL:—I take it then that the greasiness of the oil largely determines its value.

MR. AGNEW:—Yes.

MR. OBERFELL:—What test have we that determines that? I can see a relation between the body and the emulsification, but can you get an oil that has not as much of this greasiness as an other oil and get as high an emulsification with it?

MR. AGNEW:—Yes; any oil can be made to emulsify.

Digitized by Google

MR. OBERFELL:—Then the greasiness of the oil cannot be determined by the emulsification, I understand.

MR. AGNEW:— No; it is the way it is treated.

MR. OBERFELL:—How about the body?

MR. AGNEW:—The gravity, I say, has really nothing to do with it.

MR. OBERFELL:—Well, I mean the viscosity.

MR. AGNEW:—The tar base oils are higher in viscosity at the lower temperatures.

MR. OBERFELL:—The greasiness has nothing to do with it?

MR. AGNEW:—No; excepting in comparing oils made from the same crude.

MR. OBERFELL:—Then we have nothing to determine the greasiness of the oil in any of our tests, have we?

MR. AGNEW:—Why, there is nothing I know of where so many results can be obtained from a number of tests. (Laughter). That is really so. We cannot get over it. You can get flash, evaporation and viscosity almost identical every time if you have the same constant. Now when it comes to actual value,—what will it do on leather? Is it oily enough; is it rich enough in oil to take the place of fat oils; can you make an oil that is rich enough in fats to take the place of fat oils like cod and fish and those other animal oils? So that it is merely a matter of a viscous oil highly refined. That is about as far as you can go. Then, what will it do? Will another oil do as good work?

MR. VEITCH:—Can Mr. Agnew throw any light on the question of what constituent of mineral oil it is that gives harshness to the grain?

MR. AGNEW:—The lighter an oil is, that is to say the lower it flashes, the more harsh matter there is left in the oil. The higher the flash, the more you have eliminated the harsh matter. We will take Pennsylvania now. An oil that has all the light ends thrown out is naturally oilier than an oil that is lighter in gravity and has some of the light in. We will take an oil, we will say, of 400 flash; we will take an oil of 350 flash,—Pennsylvania,—made in the same still and made in the same way. Now in order to work that 350 up to 400 flash, take a

Digitized by Google

thousand barrels, you would have probably about six to seven hundred barrels left in the still; the rest had gone into light ends. Therefore the oil that is 400 flash is a great deal more valuable than the oil that has a lower flash, because it has less harsh matter in it.

MR. VEITCH:—It is a question of volatility then.

MR. AGNEW:—Yes.

MR. BLACKADDER:—I would like to ask if any measurements were made of the surface tension of these oils, especially in contact with water. I am speaking purely from a chemical standpoint.

MR. VEITCH:—The surface tension is undoubtedly affected by the presence of alkalies and acids.

MR. BLACKADDER:—Have these measurements been made by a committee at all?

MR. OBERFELL:—No, I have never made any tests along that line. I should think emulsification would have something to do with that, because as the surface tension drops the emulsification would naturally increase.

MR. AGNEW:—The actual working of the emulsification is that it emulsifies on the leather and protects the grain while drying.

MR. OBERFELL:—My idea is that it breaks the oils up in very small globules and they will go in,—it will assimilate it in other words,—while if you have a film of the oil not broken up, the surface tension enters into it and prevents the oil from penetrating. If the oil is in once, it will not drip out.

MR. AGNEW:—But take an oil which will penetrate immediately; you have harsher leather coming from the loft than you would if it—

MR. OBERFELL:—If it penetrates without working into a nice emulsion, yes.

MR. AGNEW:—If it remains on the grain and gradually goes in you have a better grain than if it goes in immediately. Oiling sole leather is for the protection of the leather while it is drying, and the emulsion does that. That is why the emulsion has been so valuable to the sole leather and why oils that emulsify take the place of cod and fish oils.

Digitized by Google

MR. TEAS:—In addition to the flash point of the oil, Mr. Agnew's inference is that the greasiness of the oil itself is at the foundation of a good leather oil. Now that means practically that the paraffine base oil is the better oil. Now you can determine whether it is paraffine or asphalt by the ultimate analysis. That is all right on the theoretical side, and yet take the standard Pennsylvania leather oil, or standard leather oil made from Pennsylvania oil, and the nearest approach, from a practical standpoint, that was ever made to it was made from a Texas oil with an asphalt base. Is that not so? The tanners say so.

MR. AGNEW:—I can say one thing: Take for instance a wool oil used for the oiling of wood. We have made oils for this purpose for many years and know that a certain amount of fatty oil is necessary to produce a proper article, but unless the mineral oil is properly treated, no amount of animal or fatty oils in addition will make a satisfactory wool oil. The mineral oil must be right, then, whatever the mixtures of animal oils may be, we have something.

This holds good for leather oils as well, the mineral oil must be properly made for leather purposes whether it is used straight or in compound.

As regards Texas oil, I am not saying anything about that; there is plenty of it. It is all right, I guess.

MR. OBERFELL:—I would like to get some expression on the point which was first brought out here, about the present methods which we have for the analysis of fats; I mean the fatty oils. I did find out from members of the committee, those who took enough interest to reply to the committee letters, that there seemed to be a general dissatisfaction with our having a definite stated method for determining the saponification value and acid value and so on and allowing them to become old and obsolete. We can get these methods from standard books on oils, but what we really need is a definite method for testing the various oils like sulphonated oils, moellons, degras and so forth. I think that would be the point towards which our efforts should extend in oil analysis. If I get a sample of sod oil and I start to value that oil I will perhaps pursue a different method or a different line of work

Digitized by Google

entirely than some other chemist, just because we have no stated procedure for that class of oils.

MR. ALSOP:—I think that was the first idea when we originally appointed a committee on oils. We ought to have a committee to do work on special oils, and not general methods, if we want to get anywhere.

MR. VEITCH:—If there is any special feature of any of these oils that calls for variations from a standard method that is the information that this association wants.

MR. BALDERSTON:—It seems to me some of us will have to learn a good deal before we can say of a given sample what kind of an oil it is.

MR. AGNEW:—That is what has always puzzled the oil men. Take, for instance, a sample of fish oil and, say, three other oils, have them mixed, analyze them and say, "What is this?" Now I used to say that I would give more for our superintendent's nose than I would for our chemist, because if it was a mere matter of guess the question would be, "Can we duplicate this oil?" The point, from my experience, is to give them something that we know will do the work; but when it comes to analyzing an oil or soap and telling what it is, I have never seen the man yet who could do it,—and we have some pretty good chemists. It is just about impossible to analyze an oil that is a mixture of several oils of different origin.

MR. OBERFELL:—Granting that all that is true, still there are lots of oils that belong to certain definite classes that we could provide definite procedure for, even granting that there are mixtures of compounded oils which are very difficult to analyze. But for certain oils that belong to certain definite classes, it seems to me we could devise a certain procedure for each. Just as we take mineral oils and try to devise a procedure for them, so we could take moellons and degras and other leather oils and handle those. It would be of more value than having our methods as we now have them for oils and fats.

MR. AGNEW:—There is no trouble in testing an oil to see if it is pure, but when you get mixtures it is hard to tear them apart. I do not know if that will ever be done or not. It is a mere matter of guesswork, with the oil man at least.

Digitized by Google

MR. LOVELAND:—I would like to know what bearing the acidity or alkalinity would have on the oil to the tanner.

MR. OBERFELL:—To me it would indicate whether the oil had been properly and carefully treated. They use acid and alkali in refining the oil, and if it is not properly removed you would assume that the oil had not been carefully treated; and I should think that the alkali, if there was enough of it, would have a harsh effect on the grain of the leather and make it, probably, dark. That is the effect of alkali if you get enough of it.

MR. VEITCH:—It seems to me with reference to these methods that the methods for emulsification should be a little more definitely described and we should use a mechanical procedure that could be readily controlled. There is too much of the personal equation in shaking in the flask, it seems to me, and the method could be improved in that respect.

Regarding the evaporation and flash, I believe it would be well if the committee could find a distillation test to replace these and give more information than either the evaporation or the flash. You will get then the knowledge of how much to distill between definite limits, and I think possibly that will give you more information than either one of these other tests. And regarding evaporation from a piece of paper, I believe that could be done in an ordinary covered dish and that would cover the objections that were raised.

MR. HOPPENSTEDT:—In calculating the amount of actual oil present in a sulphonated oil should the ash be added to the moisture and other substances outside of the oil and then deducted from 100 and the balance called actual oil? It seems to me some chemists are in the habit of determining the moisture and deducting that from 100 and calling the remainder actual oil. It seems to me that the ash should be added to the moisture and any other products that are there and that the difference should be actual oil. I would like to hear some remarks about this, because some of them contain a large amount of sodium sulphate and it is not actual oil. It does not do any actual good, so far as I can see. What I wish to get at is the actual amount of oil that the oils are sold on, because that is what you want to know. Why

Digitized by Google

should not the sodium sulphate be indicated just as well as the moisture?

MR. OBERFELL:—Many chemists do it.

MR. RIKER:—I follow Lewkowitsch word for word. He uses a very good method for determining neutral oil and sulphonated oil and the ash, and from the neutral oil and the sulphonated oil and the soap determined by the alkali in the ash the quality of the sulphonated oil can be ascertained.

MR. LEVI:—What is Mr. Hoppenstedt going to do in case he has an original turkey red oil, which is an ammonia product? As soon as you ash it the ammonium salts are driven off.

MR. HOPPENSTEDT:—Yes; well that is a point that needs consideration, I guess; a good one.

MR. NORRIS:—I think we ought to give that subject considerable attention, because at the present time there are a great many sulphonated oils on the market. We know that many of these oils are sulphonated with sulphuric acid and then washed with salt. I have found many samples in which after they had stood awhile would have a deposit of salt at the bottom of the bottle. I have known chemists to make a determination of the water in those oils and simply give the water determination. In drying it, that simply gives the water; it does not give the salt. I think as Mr. Hoppenstedt says, we should determine the ash, or determine the chlorides or some such matter, and that should be detected, because most of those oils are sold on a certain percentage of oil, say 85 per cent. oil.

MR. TEAS:—What is the average ash percentage?

MR. HOPPENSTEDT:—They vary quite a little, from one and a half to five.

MR. VEITCH:—I do not believe a determination of the ash will give all the information desired. There are other things there undoubtedly that are not oil, and one thing would be the water of crystallization of sodium and other salts that might be present. I think that matter should be called to the attention of the oil committee next year and let them give it consideration.

MR. OBERFELL:—Why would not the determination of the free fatty acids give you an indication of the amount of actual oil that is in the sample? The only possible discrepancy I can see

Digitized by Google

would be the loss due the splitting up of the glycerides in the free fatty acids, the amount of determination of glycerine.

MR. VEITCH:—It undoubtedly would give a great deal of information. I do not know whether it would give enough.

MR. OBERFELL:—You could separate the free fatty acids and weigh them and see how much you have.

DISCUSSION OF METHODS IN TANNIN ANALYSIS.[1]

The presiding officer, Vice-President Griffith, called for a report from the Committee on Rapid Cooling of Tannin Solutions.

MR. REED:—I was appointed chairman of that committee. and the committee was appointed by the Council tentatively. It did not know whether there was anything to be gotten out of it or not. We have done work so long on this subject, including the asbestos-kaolin method, that I went to work as chairman of the committee and did a little preliminary experimenting to see if I could arrive at anything worth while to give out to the committee along other lines. I have a few notes with me on this work. Mr. Oberfell I know has done some work on an entirely new method of filtering tannin solutions, which in my opinion goes along with the rapid cooling method. We have hitherto worked along the line of simply making up the solutions by the official method and cooling them off under the tap or with water at 15° or some other similar method such as allowing them to cool on the window sill, and never arrived at anything definite. I took an ordinary quebracho extract and dissolved it according to the official method. Another portion of the same extract I dissolved on the following day so that I could run the filtrations at the same time; dissolving six grams of extract in 100 cc. of water on the water-bath and pouring it directly into 800 cc. water at 20 degrees centigrade in a liter flask and made up to the mark. I found a large increase in the insoluble matters by this method as compared to the official method. Two experiments showed, by the official 4.70 and 4.70, and by the experimental method 7.65 and 7.26 per cent. insolubles. I would say that the temperature of the two solutions, was

[1] Washington Convention, A. L. C. A., Dec. 8, 1911.

Digitized by Google

brought to the same point before filtration, so that they are comparative. I tried this on another solid quebracho which gave by the official 4.41 and by this method 5.85, insolubles and on a hemlock which gave 0.81 by the official and 0.74 insolubles by this rapid method. Another quebracho gave 4.80 by the official and 6.62 by the rapid. Another 4.55 and 6.55. Then I altered the method somewhat by dissolving in 200 cc. of water on the water-bath instead of 100 cc., and obtained results that were very comparable with the official method, the official giving 6.20 of insolubles and the rapid method 6.29 on the same ordinary quebracho extract. On a partly clarified liquid quebracho I got 1.46 by the official method and only 0.17 by this rapid method.

And they don't seem to give always uniform results. Here is another quebracho by the official method which gave 6.05 and when I dissolved in 200 cc. and made to the mark, 4.42. Now, understand that all these soluble solids filtrates were apparently clear, that is, they might have a little haze, but the official and the other were practically identical in this respect. Another gave me 3.87 and 3.78; respectively, another 5.55 and 5.82 A crystal chestnut extract gave me 1.08 and 1.05 respecttively by the two methods, and a liquid chestnut 0.42 and 0.22. Another solid ordinary quebracho extract 5.14, 4.25 official and 5.64, 5.86 rapid method. Another chestnut crystal, 1.05 official and 0.90; official rapid method and a liquid 0.36 and 0.30 respectively. I made an experiment also by dissolving in 500 cc. of water on the water-bath, making up to two liters with water of 20° C. and having the official solution of the same temperature at time of filtration. Here I got by the official method 4.49 insolubles and by this rapid method 2.75. It would appear as though the amount of insolubles, especially of an ordinary Quebracho extract, depended very largely on the way it was dissolved.

MR. GRIFFITH:—There is no question but that the volume in which the extract is dissolved has a considerable effect upon the insoluble contents. That is one of the reasons why analytical results obtained in the laboratories do not always coincide with the results obtained in the tanneries. Density affects solu-

Digitized by Google

bility, and it opens up a very big question. As to how far we ought to be justified in changing a method which is working fairly satisfactorily is for the association to decide, but the closer we approximate to practical conditions in the laboratory the better it will be, the more useful the leather chemist will be to the tanner. I have always felt that the value of a tannin analysis was only a value from the point of view of comparison, but I should be very glad personally to hear the views of the members present because I am sure most of you have gone into that subject at one time or another. Of course you would have to in practical work.

MR. REED:—Just what is the interpretation of this language in the official method on the analysis of extracts? It says "Dissolve in exactly 900 cc. of distilled water at 80° C."

MR. OBERFELL:—I think you will find lots of things like that in our official method that need revision.

MR. REED:—I think that a good many variations in results may be due to different methods of dissolving.

MR. YOCUM:—A lot of the specific statements in the official method are not lived up to. Nevertheless there has been some good, established reason for specifying conditions. That is one of them,—"Dissolve in exactly 900 cc. at 80°." All right. Who does it? And if there is a variation in the result, one man doing it and another not doing it, who is responsible? The thing that must be borne in the minds of the operating chemists is to follow the method. Now if the method is impracticable it ought to be changed and established on some working basis, but the method is a method, and when we put our names to it and say that "this analysis has been done by the official method," it ought to be done that way no matter whether the method is right or wrong.

MR. REED:—Exactly; and I believe Mr. Yocum had an article recently criticising very strongly the official method.

MR. YOCUM:— In some particulars, yes.

MR. REED:—And Mr. Yocum thinks it ought to be changed.

MR. YOCUM:—I do to a certain extent. When this organization was first established I stood out very strongly against any change of the tannin method from the method that was established by the A. O. A. C. I did not believe there was any justification

Digitized by Google

for a change in the method at that time, and I do not believe that there is any justification for a general change in the method now. This organization has been in existence for eight or nine years, and it surely ought to be able now, with the membership it has and the attendance that we have at the meetings, to change methods; and I believe frankly that our official tannin method can be improved. I do not mean to change the theory of the method, but there are a whole lot of little things that got into our methods that are established and stay there somehow, so that when you commence to work under them you find they are either impossible or unnecessary.

MR. OBERFELL:—As I understand it, is not a lot of this trouble with a description of the methods, not with the methods themselves; they are not full enough?

MR. GRIFFITH:—It appears to me that the trouble is with the interpretation of simple statements. It is remarkable how many different interpretations can be put on a very simple statement, and in drawing up the official methods the various committees which worked became so familiar with the method themselves that they overlooked frequently to make certain points clear, and no doubt as we go along we shall improve upon it and make more definite our statements in the official method.

MR. REED:—I agree entirely with what Mr. Yocum said, and I think the council should this year in appointing its committees take it under consideration and appoint a committee to revise the methods along the lines that appeared in Mr. Yocum's article. It is a good basis to work upon.

MR. NORRIS:—I think it is a very important thing in making up tannin solutions when the extract is dissolved that the 900 cc. be brought up to the temperature of 80° C., especially in making up solutions of ordinary extract, and it is also very important to use papers in filtration of uniform weight.

MR. BUCHANAN:—I have been told by a friend of mine here who works for a concern that has two laboratories that they had some difficulty in getting concordant analyses from their laboratories. They got their two chemists together over in New York, worked the thing out in detail in a practical demonstration on the stock on which they were working. After that they had

Digitized by Google

no difficulty. And it occurred to me that it might be a good scheme if at some future meeting we might here have the thing tried,—extract analyses for instance run off by a committee, or by one or two chemists, that our various members might follow it exactly.

MR. FOX:—With reference to what Mr. Reed said about the official method calling for dissolving in 900 cc. of water, we all know that it is impossible to do that without some preliminary treatment. There are two or three ways of doing that, and according to the results Mr. Reed has shown a little variation in transferring will make quite considerable difference. I think that is a very important question, just bringing this extract to a condition where you can add 900 cc. of water.

MR. LOVELAND:—As to Mr. Fox's remarks on making up an extract; I think the method is a little hazy perhaps in some things. I weigh it out in a stoppered weighing bottle. I have a copper tank with a rubber hose attached, with a glass nozzle. I heat the water in the tank to 85° C., and as it comes out from the rubber hose it is at 80 or very near 80. I dissolve the extracts, putting a funnel in my liter flask with a piece of cotton fiber in the neck of the liter flask to keep air out, and dissolve the extract up with that water at 80 degrees. As far as the 900 cc. is concerned, I have to guess at that. The only way that I see to settle that question would be to have a liter flask with two marks, one at 900 and the other at 1000 cc. There have been several chemists in my laboratory, extract men, and I understand from one at least that they make extract solutions up the way that I do, and I have never heard anyone raise any objections. In visiting a number of laboratories I find that in most instances the liter flasks are like mine, and they certainly must guess at the number of cubic centimeters they use.

MR. REED:—The method I have used, is to take diamond ink and make on the flask a mark at 900 cc. It can be done very readily. Of course it will not be exact, but it is sufficiently near for the purpose.

MR. SMALL:—Another way is to use an ordinary small gummed label for numbering the flasks and to have the top of the tag at exactly the 900 cc. mark. By coating the tag with shellac it is

Digitized by Google

not rubbed off by washing, and it gives a perfectly definite 900 cc. mark.

MR. LOVELAND:—Another thing; we say in the method for tannins, "A quantity of hide-powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with 25 times its weight of water till thoroughly soaked; add 3 per cent. of chrome alum in solution." I know what that means and every other leather chemist knows what that means, but when a novice picks up this book of methods will he know how to proceed?

MR. SMALL:—This is perhaps a fitting time to bring up a matter that I had intended to present for your consideration. There are certain extracts on the market which if detannized according to a strict interpretation of the official method do not give a non-tannin filtrate which is clear, or which can be made clear by any permissible process of filtration. Moreover it frequently is the case that the non-tannin filtrates from these extracts give a test with gelatine-salt solution. Now what is the analyst going to do? Is it desirable to modify the procedure somewhat and get a clear non-tannin filtrate which will give no test with gelatine-salt, or is it desirable to adhere strictly to the procedure called for in the official method and to pass the non-tannin filtrate even though it may seem to give a test with gelatine-salt and is not perfectly clear? I have found that a clear non-tannin filtrate can be obtained in all cases by allowing the hide-powder to stand in contact with the analysis solution before putting it in the shaker. There is nothing in the official method which specifically forbids doing this. At the same time, the normal interpretation of the directions would seem to be that so soon as the hide powder is put into the analysis solution the mixture shall at once be put in the shaker and shaken for ten minutes and then immediately squeezed out through cloth. It is a fact that if the hide powder and the analysis solution are allowed to stand in contact before being shaken the resultant non-tannin figure is lower than it is if the mixture is immediately put on the shaker. A series of tests I carried through recently, show that a half hour's standing before shaking results in lowering the non-tannin value in the case of an ordinary 25 per cent. extract

Digitized by Google

from one-quarter to three-tenths of a per cent. Another half hour's standing—that is, an hour all told—again reduces the non-tannin value by perhaps one-quarter to three-tenths of a per cent. We all of us want a method which will enable us to secure concordant results, results which will be in agreement in the different laboratories. The question is, is it better to abide by a strict interpretation of the method and immediately put the analysis solution with the hide powder in it on the shaker, or is it better to allow them to stand in contact for a minimum time, say perhaps a half hour, before putting the solution into the shaker, thereby obtaining a clear non-tannin filtrate which gives no test with gelatine-salt?

MR. REED:—Would not the same end be accomplished if we had a little more acid hide powder?

MR. SMALL:—Possibly.

MR. FAUST:—I tried that and I found that to be the case. If you increase the acidity of the hide powder up to the limit[1] which is allowed—I forget the figures—you get a lower non-tannin.

MR. LOVELAND:—Could a man adhere to the official method and still run his laboratory in a practical way? For instance, if I have twelve extracts I weigh out the hide powder and start down the line, draw off non-tannins in a 200 cc. pipette and pipette until I have the twelve, then cork them up, give them a little shake, put in a shaking machine which holds twelve bottles and shake for ten minutes according to the official method. According to Mr. Small's idea, which is undoubtedly right, the man whose extract is on the table first is going to get the benefit of more tannin than the man whose extract is number 12. How are we going to get around that? We cannot pipette 200 cc., put in a shaking machine and shake ten minutes and go down the line doing that in each case.

MR. REED:—I use a flask for that purpose. Measure out 200 cc. in a flask. You can get the flask so it will drain 200 cc. and have enough for the entire analysis. I have all them measured out and put all solutions upon the hide powder at the same time.

[1] The method does not specify limits of acidity.—EDITOR.

Digitized by Google

MR. LOVELAND:—You mean drain from a 200 cc. flask?

MR. REED:—Yes.

MR. LOVELAND:—Will it drain as well as a pipette?

MR. REED:—For the purpose, yes. You can get the flask so it will drain 200 cc. exactly.

MR. VEITCH:—I do not see that exactly 200 cc. makes any difference.

MR. REED:—A little variation does not make any difference.

ABSTRACTS.

An Electric Heater for Ether Extractions. *Jour. Ind. and Eng. Chem.*, Dec., 1911, p. 929.—The apparatus described uses from 1 to 4 amperes of current on a 100-volt circuit, giving a range of temperatures from 42° C. to 135° C. This range makes possible extraction with various solvents. Good results have been obtained in use at the agricultural experiment station, Univ. of Arizona, Tuscon. The apparatus may be obtained from the Central Scientific Co.

Manufacture of Lace Leather. *Le Journal Des Tanneurs et Megissiers*, through *LeCuir*, IV, 509. Light hides are used. The liming should be done with about equal quantities of lime and red arsenic, the hides being kept in motion for an hour at a time with intervals of several hours. After unhairing and washing they are delimed by working in a bath containing 2 pounds lactic acid and 8 pounds salt, to 100 pounds white hide. They are then heated with a solution of 4 pounds alum and 5 pounds salt in 15 gallons of water to 100 pounds hide. After 1 ½ hours drumming they are horsed up for a day. After splitting the hide is drummed from one-fourth to one-half an hour in a salt solution, 8 pounds to 100 pounds hide in 15 gallons of water. The chroming is done in the drum, adding one-fourth of the amount of chrome necessary for tannage, to the salt water in the drum. After half an hour's drumming another fourth is added, and after another half hour the remainder of the chrome, the drumming being continued for 5 hours, when tannage should be complete. They are then horsed up for 2 days, then neutralized with borax solution at 45° C., and then washed. They are then drummed with degras and soap solution, to which dye may be added if required. The hides are now dried; after which they are dipped in water at 150° F. preparatory to fat-liquoring. The fat liquor for 10 hides is made by dissolving 1 pound of soap in 3 gallons of water, adding 3 pounds degras, one quart of neatsfoot oil, cooled to 180° F., when a little acid potassium tartrate is added. The skins are drummed for half an hour, then dried and oiled with neatsfoot oil. L. B.

Digitized by Google

Legal Decision against "Fiber-Leather." *Haüte und Leder,* Dec. 15, 1911. A discussion was rendered in Berlin, Nov. 30, 1911, against the "Hanseatische Vulcan-Fiber Gesellschaft," that their "fiber-leather" is not leather, and is not patented, as advertised. The company was enjoined from describing their product as leather, or naming it leather.

L. B.

Manufacture of Oils from Fish Refuse. M. Victor Cambon in *Les Matieres Grasses,* Nov. 25, 1911.—Methods have been much improved of recent years. Proportions of oil vary greatly: turbot one-half per cent.; herring and sardine from 15 to 20 per cent. In the case of sea fish which are cured, the refuse is sometimes all used as fertilizer. Sometimes it is boiled with water, the oil which floats being skimmed off. In this process a part of the oil is lost, being emulsified in the water, and a part of the nitrogen is also lost in the waste liquid. The solid residue is used as fertilizer. A much better process is now used in many of the fishery ports of Germany, Norway, etc. It is found that by cooking and pressing from one-half to two-thirds of the oil can be recovered. The residue can only be obtained by the use of solvents. The dry residue, after recovery of the solvent, is pulverized and sold as a food for hogs and poultry. If the oil is thoroughly extracted, no bad flavor is given to the meat. From a ton of fish refuse, formerly almost valueless, 500 pounds of meal are made, worth about 2.5 cents per pound; and 280 lbs. of oil, worth 5 cents a pound; the expense of heating the ton of refuse being about $4.

L. B.

Preparation of Mineral Lubricating Oils. *Petroleum Review,* through *Les Matieres Grasses.* The portion of the crude petroleum which is to be used for the manufacture of lubricants is first distilled with steam. The lighter portions thus obtained are used for spindle oils and for ice-machine lubrication. The part which remains after the removal of these lighter parts is called "reduced oil." Cylinder oils are made from this by treatment with acid, or by filtration through wood charcoal. The latter method gives lighter colored oils, but this advantage is gained at the expense of viscosity and lubricating power. For the acid treatment, the oil is placed in steel tanks, and after the addition of a small quantity of sulphuric acid, stirred by bubbling air through it. The acid thickens and blackens and absorbs many times its volume of oil. The dirty acid is allowed to settle and is then drawn off. This treatment is repeated until the oil attains the desired color. The oil is then intimately mixed with a solution of caustic soda. This part of the process, since the finished oil must be neutral, is very delicate. If any acid remains, it will blacken and any excess of alkali is almost impossible to wash out.

The oil is then washed with hot water, which at first comes off milky, but is clear when the washing is complete. The oil has now a permanent color, but it is cloudy. It is clarified by being for sometime kept warm

Digitized by Google

in shallow tanks, air being bubbled through it. The loss in treatment with acid is about 10 per cent. and the alkali and water remove 1 to 2 per cent more. Machine oils lose up to 30 per cent. in refining. California oils are heavier than those of Pennsylvania, with a lower flash point, and are very hard to wash. They are apt to contain traces of alkaline soaps, which fact does not injure them for most lubrication purposes, but makes them undesirable for cylinder oils.

Soja Bean Oil. *Chem. Ztg.*, 1911, p. 839.—Specific gravity, 0.9265; Freezes at —15° to —16°; melts at —7° to —8°; saponification value, 19; iodine value, 132 to 135. The oil contains 0.2 per cent. phytosterine; 12 per cent. saturated fatty acids chiefly palmitic and stearic; 80 per cent. non-saturated fatty acids of which 50 per cent. is an acid isomeric with linoleic, and 15 per cent. is made up of linoleic, oleic and insolinoleic acids. L.B.

Use of Fleshing Machines for Heavy Hides. *Ledertechnische Rundschau,* Nov. 23, 1911.—The writer states that the revolving spiral knife type of machine cuts the glue-stock into small pieces, whereby much of its value is lost. The heavy pressure to which the hide is subjected by the feed-rolls causes some loss of substance. The cost of a fleshing machine for heavy hides is put at 6,500 marks (about $1,150). Reckoning interest on cost, repairs, cost of power, labor of operator and loss on glue-stock, the cost of fleshing by machine is put at 0.214 mark per hide, against 0.25 mark for the same work done by hand: (5.09 cents against 5.95 cents).

Chrome Tannage. Address by B KOHNSTEIN to the Bohemian Tanners' Association, Prague. *Gerber Courier,* December 2, 1911. Chrome tanned calf-skins yield 8 to ten per cent. less area than gambier tanned skins. Sound, even, rather heavy hides from young steers or young cows are specially suited for chrome tannage, (box-calf). For enamelled chrome light cow-hides, the better grade of goat-skins and horse-hides are suitable. Because in chrome tannage there is no filling in with tanning materials or other load, the yield both in area and weight is less than in vegetable tannage. Special care is necessary in the bates and limes to avoid loss of hide substance. Unhairing is sometimes done by means of sodium sulphide, without lime. In this case addition of some carbon tetrachloride or benzine aids in the removal of fat. The pickling may be called a sort of fore-tannage. Hydrochloric, sulphuric or butyric acid may be used. Two parts of butyric acid to ten parts of salt or 1 part sulphuric acid to ten of salt may be used. One to two per cent. of alum is often added. Other tanners use alum and salt, and still others omit the pickling entirely. If the pickle does not reach the inner part of the hide, the grain of the leather may be drawn or wrinkled. If the hides are to be split, this is done after pickling. In the one-bath process of chroming, the liquor is acid at the start, and the basicity is increased as the tanning progresses. Leather made by the

Digitized by Google

two-bath process is softer and more elastic and has a lighter color, on account of the sulphur contained. Two-bath chrome heavily loaded with moellon is used for anti-skid covers for automobile tires. Dr. Kohnstein gives an unfavorable opinion of straight chrome sole except for athletic shoes and the like. He says that in Bohemia chrome belting is being made for dynamos and other uses with marked success. Various reasons are given for preferring vegetable upper leathers to those tanned with chrome, the last being that if the wearer should be shot through a chrome shoe, the wound would heal slowly!

L. B.

Annual Report of the Operations of the Research Institute for the Leather Industry. (Vienna.) Prof. B. Kohnstein. *Gerber Courier,* 52, No. 53. The average tannin content of fir bark examined was 13.02 per cent., highest 16.00 per cent. and least 9.42 per cent. Oak bark samples (chiefly Hungarian) averaged 10.4 per cent. Many samples of mimosa, from Natal and Australia showed an average of 32.92 per cent., the lowest being 26.9 per cent. The average of mangrove samples examined was 42.73 per cent., and mallet-bark 41.16 per cent.; Sicilian sumach, 27.53 per cent.; Tyrolese sumach, 18.53 per cent.; knoppern, 34.40 per cent.; valonia, 27.8 per cent.; trillo, 40.00 per cent.; divi-divi, 40.7 per cent.; hulled myrobalans, 46-47 per cent.; whole myrobalans, 27 to 36 per cent.; quebracho wood, 21.09 per cent. Quebracho extracts, solid, averaged water 20.98, tannin 66.34, reds 8.78, non-tans 3.90 per cent., ash, 0.35 to 0.60 per cent. A pulverized quebracho showed 74 per cent. tannin. Liquid quebracho extracts, guaranteed pure, showed an average of 63.12 water, 30.07 tannin, 0.89 reds, 5.92 non-tans, 0.79 per cent. ash. Chestnut extract, water 54.38, tannin, 34.10, reds 1.20 non-tans 10.32, and ash 1.94 per cent. The filter-bell method was not used except in cases where the sender of the sample expressly ordered it.

L. B.

Analysis of Fats. Dr. Prof. Baldracco. *Report to Turin Congress. The Leather Manufacturer,* Dec., 1911.

1. *Degras.*

In the Seventh International Congress of Chemists of the Leather Industry, which was held at Turin in 1904, a committee was appointed, composed of Professors Jean, Meunier, Paessler, Schorlemmer and the writer of this report, to elaborate a uniform method for the analysis of degras. This committee formulated its conclusions and presented the propositions to the Eighth Congress, which met at Frankfort in the month of September, 1906. These propositions were published in the *Collegium* of 1906, p. 304, and their prescriptions for analytical examination of degras are now in force, and no drawbacks in connection with them have been experienced. I am thinking, however, of proposing that the method of analysis just mentioned be accepted by our Congress as the official method of analyzing degras.

Digitized by Google

2. *The Yolks of Eggs.*

I propose for the yolks of eggs that the commercial analysis be adopted that was also worked out by the committee, which reported regarding degras, and which official method was published in the *Collegium* of 1906, p. 242.

3. *Tallow.*

Regarding the analysis of tallows, the analytical determinations which would indicate their value in their use in currying, are the amount of tallow, the percentage of humidity, and the percentage of foreign matter in the tallow.

It would be well, however, to fix by an official method of analysis, the qualities that should be possessed by tallow to be considered commercially suitable for use in currying.

In fact, to-day, when the industry of oleomargarine has become so extensive, we find in commerce large quantities of tallow that is very rich in stearic acid and on the other hand very poor in oleic acid. This want of oleic acid in the tallow is in my opinion the cause of ill success in stuffing leathers. It is necessary, therefore, to fix in a precise manner the limits of the proportions of the components, stearic and oleic acids, in tallows intended for use in currying.

4. *For Oils in General.*

I consider that it would also be very interesting for tanners to establish methods of analysis based on fixed data; thus, among fish oils, for example, we have in commerce, oils designated as crude oils and pressed oils. These oils have in practice the disadvantage of repelling resinous materials. We have besides, cooked oils, or what are so called, which are preferable for use in currying, because, while possessing an appreciably high acidity, they do not offer the drawback of repelling resinous matter that the raw oils do.

5. *Neatsfoot Oils.*

For these which are employed in stuffing hides and skins tanned with chrome, it would be necessary to fix exactly in what cases the determination of point of congealation should be required, seeing that this point appears to be important in oils intended for dressing the grain of leather.

Acidity in neatsfoot oils has to be considered in relation to the use to which the oil is to be put, because it has been shown that a neatsfoot oil having a higher proportion of acidity (maximum acidity 7) gives more complete and constant emulsions, while oils for dressing the grain should have a very low acidity (maximum acidity 3) in order not to attack the color nor to produce in time a dull looking grain.

It would be necessary, therefore, to unify the methods of analyzing neatsfoot oils and to lay down the analytical data that these oils should possess in relation to their respective employment in chrome tannage.

Manufacture of Sole Leather. *Gerber Courier,* 52, No. 50.—The German ox-hide which weighs about 100 pounds, is the best stock for

Digitized by Google

sole. After the hides are soaked, they are hung over a framework, pounded, allowed to drip, and then hung in the sweatpits. There are a number of different sweating systems among which is the old system of simply folding the hides together, laying them in a heap under cover, and permitting them to lie until the hair loosens. This method is dangerous since the heat developed is liable to damage the hides. The steam sweating method is the best as it is done in an air-tight room, on the floor of which is placed a steam-coil covered by a board, both being perforated to permit the steam to flow out into the room; a thermometer on the door allows the temperature to be read from the outside. By regulating the steam, temperature is held at about 75° to 85° F., the hides are hung over hangers with the grain side out and allowed to hang thus for about a day, then examined, and if the hair pulls out easily, removed from the hangers. Over-sweating must be avoided as it weakens the grain by putrefaction. The bad spots are now rubbed with fine sand or lime and the hide dehaired at once. The dehaired hide is then rinsed clean and thrown into fresh water for about six hours, where the hide, reduced by the sweating, swells again. After fleshing the hides are reeled into lukewarm water and then grained. The white weight is now taken after which the hides go to the handlers. A series of about six handlers is needed all of which are filled with acid liquors and strengthened by means of tanbark or extract. With frequent handling the hides are left in the first liquor one day with a strength of 5° Bk.; in the second, two days, about 5.5° Bk.; in the third, three days at 6° Bk.; in the fourth four days, 6.5° Bk.; in the fifth four days, 7° Bk.; and in the sixth four days, 7.5° Bk. The acid liquors plump the hides and where acid is lacking through unfavorable water conditions it may be supplied by adding lactic or acetic acid. Care must be taken not to allow the swelled hide to "fall" through too weak a liquor since hides thus deteriorated do not swell again and the results is a "tinny" leather.

From the sixth handler the hides go to the layers which consist of a series of vats filled with sour liquor. These vats are supplied with wooden frames on which the hides are spread and strewn with tanning material; usually in the first layer this dusting material is half pine and half oak bark, coarsely ground. Many tanners sift the bark in order to separate out the dust which clogs the pores of the hide. When the vats are filled, liquor is pumped in to cover the hides and after four weeks in the first layer, the hides are lifted. For dusting material the proportion needed here is about 10 pounds to 100 pounds white weight of hide; to guard against dust it is recommended to mix the bark with spent tan. The hides remain in the first layer about two months using one-half oak and one-half pine bark for dusting material; second layer about three months, dusting with two-thirds oak and one-third pine bark; and in the third layer, for three months using pure oak bark. In the third layer, it is recommended to strew the grain side with valonia dust

Digitized by Google

to produce a beautiful white grain. In the old process temperature and strength were not considered in the liquor which was used for the layers but it should be warmed to 75° to 85° F. and never permitted to go below 75° F.

The strength of the liquor can be very diverse according to the form in which the tanning material is added. Many tanners prefer a strong dusting material to a strong liquor and like to use a weak liquor while others prefer just the opposite. The latter method seems the better since in solutions the tanning material is dissolved and the hides more quickly absorb the tannin in this condition. Attention should be given to the moving of the hides in the vats since the finished product often comes to the rolling table with little hollows in the grain caused by the pressure of the bark. To accelerate the tanning it is recommended to frequently pump out the liquor, strengthen it with tanning material, warm it, and then return again to the vat. By this means a good product results and the time of tanning is shortened about two months.

In finishing, the hides are beaten on the flesh side with sticks, care being taken to avoid striking or rubbing the grain as this is likely to mar it. The hides are then hung up to dry, best over a well-aired dry floor and in bad weather in a dry room with moderate warmth and air currents. When dried to the proper condition, they are laid grain on grain smoothly in a heap, covered and weighed down with weights for about 24 hours. Both the grain and flesh sides are then brushed thoroughly to remove any particles of bark, etc., adhering and rolled. With careful rolling and correct drying a beautiful smooth and white grain is produced. The hides are then hung up again, dried thoroughly, and rolled once more. L. A. C.

Frozen Leather. *Gerber Courier*, **52**, No. 47.—During the winter leather, in drying, is apt to become frozen especially where no well equipped drying loft is provided. Such leather becomes weak and limp if thawed out too rapidly. In freezing the water in the hides which have been hung up to dry, is forced out by the freezing and stretches apart the hide-fiber. The wetter the hides therefore the more demoralized they will be by the frost.

The author calls attention to the incorrect treatment of rushing the frozen leather into a warm room and advises that the best method is to allow the hides to hang as they were and to tightly close all openings to the outside air. If this is impossible it is then best to place the leather in a heap in a room where the temperature will not fall below the freezing point and cover it with a cloth. In case the leather rolls up, it should be moistened before the roll becomes greater than is customary; it will thus become firmer throughout.

Some upper leather and especially sheepskins for lining purposes are aided by freezing since the leather becomes white and plump and also is of a bright color, though the durability is somewhat lessened.

L. A. C.

Digitized by Google

Leather Fats and Oils. G. SCHNEEMANN from *Chemisch-Technische Fabrikant* through *Ledertechn. Rundschau*, 1911, 330-3.—English products bring a higher price in the foreign markets than German wares, largely because of more attention being given to attractive package; this is an important element and must be reckoned for in manufacture. The technology is simple. Steam jacketed kettles, one for yellow and one for black fats are best for melting, with mechanical agitators when over 120 kg. capacity. Careful laboratory examination of raw material is to be recommended. Leather fats (as distinguished from oils) are of salve consistence and best suited for leather in constant use making it appear well and rendering dust-proof. Some 15 recipes are given of these fats, containing paraffin or ceresin together with various plant, animal and mineral oils. These are melted at not over 80° C. and poured out at 50-60°. For the bright yellow vaseline fats, the mineral oil employed is de-bloomed with 1-1½ per cent. nitronaphthalene. A pure black with minimum nigrosin is obtained by adding sufficient yellow or brown aniline dye to compensate the blue present. For fat soluble nigrosin, 2 parts nigrosin are stirred at 60-70° into 10 parts of olein or stearin according as liquid or solid black is desired. Double space in the kettle is required for frothing. An artificial degras may be made by heating seal oil on the steam bath to 150° C. and leading a current of air through until a sample on cooling is syrup. After cooling to 60-70°, 10-15 per cent. warm water containing 0.1 per cent. soda is stirred into uniform emulsion.

Leather oils are more penetrating than fats and are used for old stock or leather that is occasionally used. Nine recipes employing principally marine oils, vaseline oil, spirit and birch tar oil, are given. The ingredients are heated together at not over 60° C.

W. J. K.

The Composition of the Refuse Solid Scum from Puering Lamb Pelts. G. EBERLE AND L. KRALL, *Collegium*, 1911, 445-9.—The material investigated was the solid refuse remaining on the knife after scraping the pelts from the dung bate. Several kilos of this substance from a glove leather factory were examined. The analysis gave

Water	29.7
Fat (ether soluble)	42.0
Fatty acid (fixed by lime)	6.6
Ash	3.5
Water soluble albumen	3.8
Hair and insol. albumen	14.4
	100.0

The ash was largely lime, 2.00 per cent. CaO. The fat extracted by ether varied from 42.54 per cent., according to moisture of sample and was yellowish, of salvy consistence; its constants were: iodine number

Digitized by Google

31.6, acid number 9.3, Hehner number 91.9. Cholesterin could be identified in its saponification product. Lime salts of unsaturated acids are somewhat soluble in ether, and the extracted fat was found to contain 0.442 per cent. CaO.

The residue from the ether extractions, after treatment with HCl gave additional fat of 6.6 per cent. on ether extraction. This fat acid had an acid number of 74.3. The soluble albumen was determined by extracting the dried scum (after removing the fat by ether) with luke warm water. The evaporated residue gave a nitrogen content agreeing with albumen. The scum therefore consists largely of a fat resembling wool fat with similar constants. A sample of the fat was sent to Dr. Fahrion for examination who reported:

	Per cent.	Iodine No.
Unsaponifiable (alcohols)	47.6	27.3
Fatty acids (sol. in petrol. ether).....	39.3	30.2
Oxy-acids (sol. in ether)	13.5	13.4

He concluded the sample to be either wool fat or a closely allied substance. W. J. K.

The Valuation of Cold Soluble Quebracho Extract. W. APPELIUS. *Ledertechn. Rundschau,* 1911, 377-80.

To correctly value an extract, besides the usual returns of the official methods of analysis, the solubility and weight giving power should also be regarded. In this research, the author compares results given by two clarified, cold soluble extracts (1) sulphited, (2) clarified without sulphite, by Dr. Redlich's patent.

The original extracts analyzed:

	Direct non-sul.	Computed sulphited	Computed non-sul.	Direct sulphited
Tanning substance	36.1	31.7	42.7	37.1
Soluble non-tans	6.6	10.8	7.7	12.6
Insoluble	0.0	0.2	0.0	0.2
Water	57.3	57.3	50.1	50.1

Analysis is always made of liquors of 0.2 to 0.4° Be, while in practice the more concentrated liquors employed may give sediments. Solubility determinations of the above extracts according to Paessler (abstract this JOURNAL, 1908 [3] 358) showed as utilization ratios 100 and 94-97 per cent. for the non-sulphited and sulphited extracts respectively. To compare the weight-giving power, hide powder was shaken with 6 per cent. liquors, washed, dried and weighed; the filtrate was also examined.

	Per cent. gain		Per cent ext. absorbed			
			hide = 100		extract = 100	
	non-sul.	sulphited	non-sul.	sulphited	non-sul.	sulphited
Unchromed hide..	56.2	28.2	82.3	44.0	48.3	22.9
Chromed hide	65.3	34.4	69.8	44.6	40.9	23.2

Digitized by Google

These results are in favor of the non-sulphited extract. Another series of experiments was made in the laboratory tannage of 75 gm. portions of pelt. A croupon slightly fore-tanned with pine was halved and corresponding strips from each half used for the sulphited and non-sulphited extracts. The extent of tannage was ascertained by nitrogen determination.

Found in leather of 18 per cent. water:

	From non-sulphited ext.		From sulphited ext.	
	hide subst.	tannin absorbed	hide subst.	tannin absorbed
After 3 days.....	48.9	31.9	59.6	20.0
6 days.....	43.8	37.0	57.9	21.7
10 days.....	43.3	37.5	52.3	27.3
13 days.....	44.4	36.4	55.1	24.5
17 days.....	43.3	37.5	53.4	26.2

These results confirm what was observed, namely that the non-sulphited extract gave a denser deposit on the fiber, resembling an untreated direct extract. A hot water test according to Fahrion (abstract this JOURNAL, 1909 [4] 60) gave water resistances of 72.3 (non-sulphited) and 42.2 per cent. (sulphited) for the above leathers. The colors yielded by each extract were the same, a light leather brown.

W. J. K.

The Composition of Tannin. W. STEINKOPF AND J. SARGARIAN. *Ber. deutsch. chem. Ges.*, 1911, [44] 2904.

Iljin (Ber. d. chem. Ges., 1909 [42] 1731) purified commercial tannin and found higher carbon percentage than commonly assumed. He found C 54.13 per cent., H 3.22 while digallic acid requires C 52.13, H 3.41. The authors have repeated Iljin's work but cannot confirm his remarkable results. Tannin acid from Kahlbaum, Schuchardt, Schering, Merck and de Haën, re-purified according to Iljin gave by combustion 52.87—52.53 per cent. C, 3.92—3.56 per cent. H.

W. J. K.

The Composition of Tannin. L. F. ILJIN. *Ber. deutsch. chem. Ges.*, 1911, [44] 3318. Tannin purified by the author's process (ref. above) is extremely hygroscopic and sufficient moisture may easily be retained to lower the carbon content to the values quoted by Steinkopf and Sargarian above. Special precautions were taken in the author's analyses to exclude moisture. W. J. K.

PATENTS.

Preparation of Hides for Tannage. French Patent No. 432,387 PAUL EUGENE CHAMBARD, France. The hide is treated with an acid solution containing nitrites, thus liberating oxides of nitrogen, and then with

Digitized by Google

a solution of a sulphite, bi-sulphite or hyposulphite, by which means SO_2 is liberated on the hide fiber. The process it is claimed produces a very satisfactory plumping.

Evaporating Apparatus. U. S. Patent 1,012,523. CHARLES CORNE, New Orleans.

CORRECTIONS.

In the December issue, Report on Leather Analysis, p. 566, line 14 should read: "Place the two residues of A together, and the two," etc. Line 13 from bottom, 60° C. should be 50° C. P. 568, erase "other extract" from table heading. P. 579, line 6, change "at least six" to "from 8 to 10."

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VI of the JOURNAL, for 1911, bound in cloth or half morocco, are now ready, Volumes I, II, III, IV and V in uniform binding may also be obtained. Price $6 per volume delivered. Bound volumes will be exchanged for complete sets of unbound numbers at the rate of $1.20 per volume delivered. Missing numbers will be supplied at 25 cents each. Unbound volumes for exchange should be well packed and sent to the Manager at Ridgway, Pa., expressage being prepaid at the "printed matter" rate.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII MARCH, 1912 No. 3

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

CHANGES OF ADDRESS.

Robert W. Griffith to Hotel Somerset, W. 47th St., New York, N. Y.

N. P. Cutler to 44 Montrose St., Newton, Mass.

Douglas McCandlish to 765 Maryland Ave., Milwaukee, Wis.

George E. Byford to 422 Sixth St., South Boston, Mass.

Cudworth Beye to c/o National Association of Tanners, 30 N. La Salle St., Chicago, Ill.

DIED.

John O. Pierson, an Associate Member, of Buffalo, N. Y., Jan. 30, 1912.

BOUND VOLUMES OF THE JOURNAL.

Copies of Volume VI of the JOURNAL, for 1911, bound in cloth or half morocco, are now ready. Volumes I, II, III, IV

Digitized by Google

and V in uniform binding may also be obtained. Price $6 per volume delivered. Bound volumes will be exchanged for complete sets of unbound numbers at the rate of $1.20 per volume delivered. Missing numbers will be supplied at 25 cents each. Unbound volumes for exchange should be well packed and sent to the Manager at Ridgway Pa., expressage being prepaid at the "printed matter" rate.

NOTICE.

The following periodicals are secured for the JOURNAL either by exchange or purchase. We desire to have all periodicals at our disposal which contain matter suitable to be reprinted or abstracted, and therefore ask members (especially foreign members) to advise us of any additions to this list which may seem advisable.

DOMESTIC.

Shoe and Leather Reporter, Boston.
Hide and Leather, Chicago.
Leather Manufacturer, Boston.
Shoe and Leather Weekly, Chicago.
Chemical Engineer, Chicago.
Journal of Industrial and Engineering Chemistry.
Journal of the American Chemical Society.
Chemical Abstracts.

FOREIGN.

Journal of the Society of Chemical Industry.
The Leather Trades Review, London.
The Leather World, London.
Journal of the Royal Society of Arts.
Der Gerber, Vienna.
Gerber Courier, Vienna.
Der Ledermarkt und Collegium, Frankfurt a. M.
Die Lederindustrie und Ledertechnische Rundschau, Berlin.
Zeitschrift für Angewandte Chemie, Leipzig.
Zeitschrift für Chemie und Industrie der Kolloide, Dresden.
Le Cuir, Paris.
La Halle aux Cuirs, Paris.
Le Marché des Cuirs, Paris.
Les Matieres Grasses, Paris.
La Conceria e la Calzoleria Meccanica, Turin.

Digitized by Google

THE CHARACTERISTICS AND COMMERCIAL ADAPTABILITY OF HIDES.[1]

By John H. Yocum.

While it is not advisable to write for technical societies articles which are based on commercial conditions, yet because of the fact that so far in the literature of the tanning trade no data are on record bearing on the character and condition of hides, I have felt it worth while to bring before this organization and have recorded for reference the varying conditions and character of the raw material of the tanning industry, particularly in view of the fact that the hide represents from 60 to 70 per cent. of the value of the resulting leather.

In using the term hide, I refer to those pelts which are usually worked into heavy leathers, as the trade distinguishes lighter pelts by the term skins or kips. Hides come to the tanner in two general conditions, dry, and green salted; there is an intermediate condition generally known as dry salted, but as there are relatively few hides on the market in this condition and as they are worked in the same manner as are the green salted hides, they will be included under green salted hides.

Dry hides are the hides that are taken off, as a rule, on the ranch or at some distance from easy transportation points, and when taken off the animal are usually hung flesh out and permitted to dry in the sun until the 70 or 75 per cent. of moisture normally in the hide when taken off is reduced to 8 or 10 per cent., and the pelt itself changed into a hard and impervious horny substance. During the drying operation, if conditions are not suitable for rapid drying, bacterial action occurs, which liquefies the fiber of the hide. This, when it reaches the tanner or selector, is known as a sun burn, and during the soaking operation these so-called sunburned spots usually drop out. Sometimes the selector can determine from the appearance of the dried hide the extent of the sun burn, and other times the extent of the sun burn is only determined by the tanner during the soaking and stocking of the hides. Such hides come out and go into

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec., 1911.

Digitized by Google

leather of the selection known as scabs and rejects, or go to pieces in working.

In trade parlance we have River Plate hides, or straight hides, and common hides. These two names refer to practically all the dry hides coming from South and Central America. The straight hides are hides shipped from Argentine and Uruguay known as Buenos Ayres and Montevideos, taking their name from the point of shipment; these hides are range cattle raised under similar climatic conditions to the Texas hide in the United States, but are not branded so heavily as are the range hides of the United States, the prevalent brand being the result of wire branding which does not occasion the formation of as much scar tissue as does the stamp brand of the States. These hides are regarded as the best of dry hides, and are largely worked into non-acid and the better grades of acid hemlock.

Common hides take their names from the different ports from which they are shipped or the neighborhood in which they are taken off, such as Puerto Cabellos, Maracaibos, Caracas, Costa Ricas, Central Americas and Orinocos, and have varying characteristics as to plumpness, quality of grain and ability to make gain of leather. They are worked into acid hemlock in its cheaper grades, and the cheaper grades of non-acid hemlock.

Other dry hides come into the market such as Chinas, dry and arsenic cured Buffalos from India, dry Californias, fallen Texas, etc., each having a different value depending upon the character of the skin of the cattle as determined by the climatic conditions of the country from which they come. This, for instance, can best be explained by the selection known as Mountain Bogotas as against Orinocos; the Mountain Bogota cattle, being raised at high altitudes and in a comparatively cold climate, are much plumper than are the Orinocos which are raised in about the same latitude but at low elevations.

Practically all the dry hides coming into this market are prepared for tanning by the sweating process, whereas practically all the salted hides are prepared for tanning by liming. The dry hides, as a rule, go into acid and non-acid hemlock sole leather, the salted hides going into union and oak sole, harness and upper leather, although some are worked into slaughter hemlock sole.

Digitized by Google

To the tanner it is essential that the hides worked by a given method of procedure in the tannery should be similar in weight and character, and it is therefore necessary for him to know, in the purchase of hides so as to turn out a given character of leather, the characteristics of the hides from different localities. Therefore, a tanner making acid hemlock from Indian Buffalo hides will pursue a different method in the treatment of the hides in the tannery from that which he would use in tanning acid hemlock from hides obtained in Venezuela or in Central America; he would also have to pursue a different method of treatment for hides from Buenos Ayres or Montevideo. Buenos Ayres and Montevideos are sufficiently like Texas to be worked together; Central Americas and Venezuelas can generally be worked together; Chinas are so various in character as to make it a matter of judgment what other hides can be worked with them successfully.

Dry pelts coming into this country and weighing over 12 pounds in the dried condition are known as hides. Pelts weighing in the dried condition between 12 and 5 pounds are known as kips; under 5 pounds in the dried condition are known as calf skins. Selections are made for hides and kips, hides tainted on both sides, badly worm-cut on both sides, sore shoulder or pox on both sides, sun burns and damage in shipment, no selection being ordinarily made for grubs, ticks or cuts. Practically all these hides are branded.

SALTED HIDES.

The salted hides that are imported from South America come under three selective names: Frigorificos, Saladeros and Mataderos. The Frigorificos, as the name indicates, are the hides taken off cattle, the meat of which is shipped out of Argentine as frozen meat. The Saladeros are the hides taken from the smaller packing establishments throughout Argentine and Uruguay. The Mataderos are the hides taken from the village butcher shops and the larger ranches, which are brought into the market in the salted condition. Few Mataderos come to this country because of their poor take-off; the Saladeros take-off is about equal to our country take-off, a little better if anything, while the Frigorifico is equivalent to our large packers' take-off. These

Digitized by Google

hides are almost all wire branded, and in that respect do not compare with the native selection in the United States. Practically all of the Argentine and Uruguay hides are staggy, that is, thick in the belly and neck, and comparatively thin along the backbone.

Other green salted hides imported into this country are of two types: such cow hides from the north of Europe suitable for buff and lace leather, and such heavy steer hides from the north of Italy, from Switzerland and France, as are suitable on account of their spread for carriage and furniture leather, and on account of their plumpness for heavy sole, belting and harness leather. No European hides coming to this country are branded, but many have prod marks which are more harmful to the grain than the wire scratches on our natives. The season for grubs varies on the Continent, and is not uniform for North Italian spready hides as against Swedish cow hides, but as a rule, is much later in the year than the grubbing season in the United States. In purchasing such hides, the rule is to make a grub selection at all times by the agent or factor taking up the hides. No general rule as to dating of grub allowances is made on foreign hides as is the case in the United States.

Another type of hide coming into the United States is known as the Anglo-American, which is the hide taken from American cattle shipped to England, the hides being returned here. These are of the same character as American hides, their seasonable take-off being from 30 to 40 days behind that of this country. However, these hides are short shanked, and for this reason command a slightly better price. These Anglo-Americans are subject to the same brand and grub selections as are our American packer hides. Some of the dry hides from the United States are sold under the term of short shanked, which means that the hide is not taken off from the knee down. In England these trotters are prepared in much the same way that pig's trotters are in this country, and are then dried and sold. For this reason, the Anglo-American hide is from 3 to 5 pounds less in weight as against a like hide here, because of the knee trim.

The green salted hides sold in this country are generally known commercially from their source as packer hides, small packer

Digitized by Google

hides and country hides. The distinction between many of the small packers in the character of the hide that they produce and that of the "big six" is simply a matter of quantity. Many of these small packers kill the same character of cattle and exercise the same care in the take-off as do the "big six," but because of the quantity killed by the larger packers they are able to give a better selection as to weights, conditions, brands and grubs than is possible for the small packer to do. There are, however, some of the small packers who take off poorly, and therefore these hides must be thrown into the country hide selection. The country hides are the hides taken off by small local butchers, the hides being salted without regard to selection, and subsequently sold to a dealer, who, after collecting from a number of the country hide butchers, makes a general selection for grubs, brands, steers, cows, bulls and weights. Among most of the small packers, however, a realization of the value of selection exists, and natives and brands, cows and bulls are packed separately, so that the tanner may purchase from them hides of a good selection suitable for a tanner's needs.

The mode of packing or curing of hides in the United States among the larger packers as well as the smaller packers, after removing and washing down the hides, is to stage the hide and permit the excess of water from the washing down to drain off. This washing down of the hide assists in the removal of the blood and manure and in a way prevents salt stains. It is important in this connection that the packer, to prevent salt stains, should use salt which has been crystallized, as it has been found that mine salt not only contains iron which will cause discoloration in the leather, but in the process of mining, the dynamite used for dislodging must be exploded by caps and small wires made of copper, which, if left in the mine salt, will cause discoloration of the hides, and, for certain purposes, make the hides less valuable. Packer hides after draining, are selected and placed in packs in which the moisture remaining in the hide furnishes sufficient water for the dissolving of the salt placed thereon, so that the salt will form a pickle and partially taw the hide. Ordinarily from 600 to 1,000 hides are placed in the pack, dependent upon the weight of the hide; the time from which

Digitized by Google

the last hide is placed thereon until the cure is effected ranges from 30 days upwards. No packer's bed of hides should be taken up, if proper weights are desired, until at least 30 days have elapsed from the time the last hide went into pack.

The selections of packer hides, as adopted by the packers, are as follows:

Spready Steers, 6 feet 6 inches and over on stuck throats; 6 feet 8 inches and over on cut throats, measured immediately behind the brisket; suitable for patent, enamel, carriage and furniture leather; selection for grubs; usually sold as of June 1st to January 1st.

Free of Brands or Native Steers.—Heavy steers, 60 pounds and up; spready selection taken out between June 1st and January 1st, remaining in January 1st to June 1st; grub selection, January 1st to June 1st. This carries the hides from 50 to 60 pounds at 1 cent less. No. 2's of each at 1 cent less. Cut throat hides ordinarily sell for ¼ cent less than stuck throat hides. Hides of the native selection on steers below 50 pounds will ordinarily go into native cow hides, as the extremes (under 50 pounds) would sell for 2 cents a pound less than heavy natives, and the packer ordinarily puts these among the cows.

Free of Brands or Native Cows.—The packer makes a selection of 25 to 45 pounds on these, which are called extremes, 45 to 55 pounds which are called buff hides, and 55 pounds and up which are called heavy cows. The extremes are used in the shoe leather and lace leather trade; the buffs almost exclusively in the shoe upper leather trade, either in chrome grains or patent grains, whereas the heavy native cows are used in the belting leather trade and in the furniture and carriage leather trade. A native hide in the United States is free of brands, or is reported free of brands by the agent taking up the hide. All hides of the packers should properly be taken up by an agent representing the tanner. It follows that there are a few branded hides found among the natives by the tanner, but this results from the fact that by examining the hide on the flesh side only it is impossible to determine a wire brand or a brand that has not penetrated the hide to such an extent as to show on the flesh.

Texas hides are sold under the terms of heavy, light and extra

Digitized by Google

light. They are all branded, and no selection is made other than for weights and the allowance for grubs. They go entirely into the sole leather trade.

Butt branded steers are steer hides which have been branded on the hip or butt. Ordinarily these show but one brand. They are sold 60 pounds and over; 50 to 60 pounds at 1 cent less, No. 2's of each 1 cent less. These go exclusively into the sole leather trade. The extra light, under 50 pounds, are usually thrown in among the branded cows.

Colorados are steer hides which are side branded. No distinction is made if the hide happens to have a butt brand and a side brand, or two side brands, and as a result, clear sides from Colorado hides do not obtain in the same proportion as they do from butt brands, and the brands are usually of a very much larger area and the scar tissue much thicker. It is the habit among some packers to select the Colorados which are plump and sell them as Texas, but the Colorado hide is not from the same animal that the Texas hide comes from; the range Texas cattle are smaller, and have thicker and plumper hides, and are able to produce sole leather of a character which Colorados will not make. All these hides go into sole leather.

Packer branded cows sell 25 pounds and up flat, except for grubs.

Country native bulls are selected in such a manner that the 25 to 45 pound bulls are thrown in with the cows. The 45 to 60 pound bulls are thrown in with the cow selection of buff hides. The 60 pound and up native bull hides are sold as such. Packer native bulls are sold all weights, generally flat; some packers allow a selection for holes.

Packer branded bulls are sold as such, flat, from 25 pounds up, and usually go into sole leather.

The tare allowance on packer hides in Chicago and western points is determined by what is known as the sweep tare, that is to say, the agent acting for the tanner taking up the hides picks out 10 hides which are weighed. The salt is then thoroughly removed by sweeping from both flesh and hair side of these hides, they are then reweighed, and the difference determines the tare allowance for that pack. However, if the seller-man

Digitized by Google

acting for the packer, or the broker acting for the tanner, are dissatisfied with this result, 10 additional hides are taken and treated in the same manner, the average loss on the 20 being used as the tare allowance. In New York and other eastern points, the tare allowance is a matter to be determined at the time of the making of the contract, as for instance, July natives may be allowed 1½ pounds tare, whereas February-March hides of the same kind would be allowed 2 or 2½ pounds because of the longer hair and its ability to absorb the finer particles of salt.

The grubbing conditions established by the packers are as follows:

Native steers are permitted to be grubbed and a grub allowance made between January 1st and June 1st of each year, which is done by sample.

For native cows, the grub allowance is from January 1st to June 1st.

Bulls, both branded and native, are not selected for grubs.

Texas steers, grub allowance, November 1st to June 1st.

Branded cows, grub allowance, November 1st to June 1st.

Colorados, grub allowance, December 1st to June 1st.

Butt brands, grub allowance, January 1st to June 1st.

These tare allowances and grub allowances have been forced upon the leather trade by the packers. In reference to this statement, it is well to call your attention to the fact that the latter part of December native hides will always run grubby, and the early part of June native hides will always run grubby. The weakness of establishing an absolute breaking point when allowance for grubs is made is that on the last day of December no grub allowance is made, whereas on the first day of January it is made. Oftentimes it happens that late Decembers and early Januarys will run 25 per cent. grubs, and thus at the breaking point the first of January, a difference in the price per pound on selections or ¼ cent per pound on the whole purchase of hides is sometimes made, depending upon the condition of the market. This explains why late Decembers as a rule do not sell at as high a price as early Januarys, and also why late Mays are usually valued higher than are early Junes.

On account of the fact that the grub allowances and tare

Digitized by Google

allowances are such important items to the tanner, it is always advisable to have these allowances determined at the time the hides are taken up. Not only is this advisable because of the above mentioned facts, but it is always advisable because of the fact that packs will come up which contain more moisture, especially in February and March, than is proper, causing the hides to lose an excessive amount of weight from the time of take-up to the time of delivery. The broker when taking up hides should refuse to take up a pack when he finds the conditions such as are not justified, and should demand that before acceptance the hides coming out of pack shall be staged. Packer hides should not be permitted to be taken up and to lie for any considerable time if it is desired to make even colors in the finished leather, for the reason that salt stains will invariably occur from this procedure.

Another point in connection with the taking up of hides is that the tare allowance should be determined before the hides are selected for lights and heavies. If this tare allowance is not determined first, then the breaking point of the scales, as the hides come out of pack, is necessarily not established. The New York practice is much better in this respect than is the western practice, because in the New York practice the tare allowance is established in the contract, whereas in the western practice, it is necessary to take a number of hides, 10 or 20, out of pack as near an average as possible, before the tare allowance can be determined. Suppose the tare allowance is estimated, allowing 1 pound per hide, the scales will then be broken at 51 pounds for lights and 61 pounds for heavies. If it then happens that the allowance is established by sweeping at 2 pounds per hide, or 52 pounds and 62 pounds, then there is a considerable proportion of the hides bought by the tanner which are really of the lighter weight, paid for by him as being of the heavier weight at 1 cent a pound difference because the breaking weights had to be determined after some of the pack had been selected. This is an important item to the tanner, and one which necessitates careful consideration and investigation, and one in which the variation of a pound, whether 61 or 62, may make $^1/_{10}$ of a cent a pound difference in the net price of the hides.

Digitized by Google

Country Hides.—The selections under country steer hides are natives, No. 1 and No. 2, 60 pounds and up; No. 1 and No. 2, 50 to 60 pounds; under 50 pounds going into extremes and buffs. Native cows are selected as extremes, 25 to 45 pounds; 45 to 60 pounds, buffs; 60 pounds and up, heavies. In this connection, it might be well to state that in country hides, bulls under 45 pounds will go into the cow selection of extremes; bulls from 45 to 60 pounds will go into the cow selection of buffs; 60 pounds and up are sold as bulls. Country branded bulls are sold as such, 25 pounds and up. It therefore rests with the tanner or the tanner's representative to see that he gets the selections which he buys.

Ordinarily all seasons take-off of country hides are sold to the tanner subject to a grub selection. This grub selection means that any hide having one or more grubs that are open from the flesh to the grain is a No. 2; so also a cut more than 6 inches in from the edge of the hide makes it a No. 2, provided the cut passes through the hide. In some sections country hides are classified as No. 2 when containing 4 or more grub holes; all packer hides are No. 2 when containing 5 or more grub holes. The ordinary term used on contracts is "cuts, grubs and No. 2, 1 cent per pound less"; this applies to both heavy and light selections.

Country hide selections:

Native steers, 60 and up, No. 1 and 2; 50-60, No. 1 and No. 2.
Branded steers, (both side and butt) 60 and up, No. 1 and No. 2; 50-60, No. 1 and No. 2.

	Extremes	Buffs	
Cows, light steers and bulls, natives	25-45	45-60	60 and up
Cows, branded	25 and up	flat for weights	
Bulls, natives			60 and up
Bulls, branded	25 and up	flat for weights	

It might be well in closing this to call the attention of the chemists here to the different possibilities of making leather from different kinds of hide. Dry hides will contain from 60 to 75 per cent. of hide substance, while green salted hides will contain from 22 to 30 per cent. of pure hide substance. These variations are due first, to the condition of the dry hide and its length of hair and cure, and on green salted hides, to the seasonable take-off of the hide, cure and condition, there being at least

Digitized by Google

15 per cent. difference between the weight of the hide taken off the same animal in June and July as against February and March. This may be explained by the length of hair, manure and general weakness of the hide at the end of the winter.

It is advisable, in all cases, in comparing hides, to depend upon the percentage of white weight, *i. e.*, the weight of the hides going into the liquor, as a measure of the relation of the hide resulting from seasonable conditions as well as take-up. It is admitted that white weight does not determine scratches, grubs, brands or other imperfections of the hide, but it is a measure of the hide buyer's ability to purchase properly for the tanner's use, so that the tanner may obtain the highest return from the purchased weight of hides; this factor can be so accurately determined that the selling weight from the white weight will not vary more than 1 per cent., provided the tanning operations are uniform.

DISCUSSION.

MR. GRIFFITH:—I am sure we all feel very much indebted to Mr. Yocum for his very excellent paper on a phase of the tanning industry which is not very popular amongst chemists. In fact I think it is the duty of the chemist to investigate further than he does, or further than the opportunity he usually has, into the question of the raw material. It is of prime importance to the industry as a whole, and to the leather chemist in particular, because without the hide of course there would be no leather, and without leather we should have no leather chemists.

The source and supply of hides is becoming a very pressing matter, and I have no doubt we shall hear something about that question when we listen to Mr. Lockwood's paper.

I should like to ask Mr. Yocum in regard to dry hides if he has observed whether tanners are getting away from the sweat process and going in for the use of sodium sulphide and lime in preference to it. And also in regard to salted hides. The great difficulty with salted hides, especially as far as the color of leather is concerned, is salt stains. I have wondered if the difficulty of salt stains as a whole could not be overcome by using a better grade of salt than the packers use. The common method

Digitized by Google

of salting hides in Chicago in some of the packing houses is to spread the salt over the hide and shake it off and brush that salt up and use it over again. Now in that process the salt, which is rock salt in large crystals, becomes coated with albuminous matter, which carries of course a large quantity of blood in which there is good deal of iron, and it seems to me it is rather obvious that the efficiency of the salt is considerably affected by using over and over again, simply because it is covered and its action is prevented by the albuminous coating that it receives from passing over so many hides. I am sure Mr. Yocum will be only too glad to give us the benefit of his observation and experience in hides, and if any of you have any questions I am sure Mr. Yocum will be glad to tell you what he knows.

MR. YOCUM:—In answer to the chairman's remarks, I would say that if hides are taken out of pack and resalted, ordinarily one gets salt stains. It is claimed that this is due to dirty salt, but I have noticed that resalting even with clean salt will produce a greater quantity of the stain in resalted hides, than if these hides were worked fresh. The claim that the iron in the blood is the cause of salt stains has never been disproven, and I have considered this was the cause of salt stains. A fresh hide,—that is, a hide immediately out of pack,—worked immediately, will not ordinarily show salt stains; however, if that hide is permitted to lie awhile or resalted it will ordinarily show salt stains. These stains seem to appear in the locations on the hide where opportunity has existed for the drying out of the hide. There is a certain concern in New York,—hide brokers,—who advise that hides should be, when they are resalted, resalted with clean crystallized salt. It is true that in using the crystallized salt, the hides do not show as much salt stain; so likely, judging from that, the resalting operation has something to do with salt stain, and it is likely that the added salt stains caused by resalting are due to the condition of the salt. I do not think you are quite correct in saying that the albuminous matter covers up the granules of the salt, say mine salt, to any extent. Probably these granules act as a center to which, for some unknown reason, the iron and other staining qualities concentrate themselves.

I have had occasion in the last 4 or 5 years, to notice stock

Digitized by Google

with a nasty stain penetrating the hide straight through,—it might be as big as a half dollar and it might be larger,—and I discovered that it was due to the copper wires used for the explosion of the dynamite in the mining of the salt. This wire changes to copper chloride and acts as a sort of copper tannage or a tannage which, after the vegetable tannin strikes it, changes to a black color which cannot be bleached out.

MR. BEARDMORE:—I would like to ask Mr. Yocum if he has ever noticed any bad effect on the hides from the metal tags that the hide dealers put on? The reason I ask the question is that I have had hides that were tagged with a zinc tag which had eaten a hole right through. A spot will drop out about as big as a fifty cent piece. That is only with the zinc tag; the tin tag does not affect it.

MR. CONNELLY:—I would like to ask Mr. Yocum if he thinks that the seasons of the year have anything to do with the salt-staining of the hide. I remember once in particular some hides coming out of our yard that had only been out of the packer's cellar seven days, and they were badly stained. We seem to get so many more in the summer than the winter that I wondered if the season of the year didn't affect them.

MR. YOCUM:—How long had they been packed?

MR. CONNELLY:—I do not know that. Not over thirty days.

MR. YOCUM:—It is quite true that the tendency to salt stain is increased as the weather gets warmer, that is, there seem to be more salt stains in summer than in winter hides, but I do not believe that this is due to any other cause than the fact that the hides in the summer are not as well washed and cooled as they drop into the cellars as they are in the winter time. With February-March hides a great deal more care is taken to wash them down because of the manure on them. More care is exercised in washing down dungy hides, than on June or July hides, and on account of the temperature of the water and the cellar itself, the hides are cooler as they go into pack. The result of the extra washing is that the blood is then removed from the hides; and the result of the cooler temperature as the hides go into pack is that less opportunity for chemical change exists, and consequently less opportunity for salt stain. However, the in-

Digitized by Google

stance Mr. Connelly cites may be due to the use of dirty and old salt.

MR. BALDERSTON:—I would like to ask Mr. Yocum another question in line with what has just been said. A number of articles have recently appeared in European journals on this question of salt stains, giving a large number of causes to which they are attributed. I cannot now state many, but there are at least a dozen causes and more than half of them are due to substances used in denaturing the salt, which does not interest Americans; but there is one which Mr. Yocum has mentioned and I would like to ask his idea about it. It is said that the blood remaining in the hide becomes a center of bacteriological action which proceeds even in the presence of the salt. That is, there is some sort of chemical action, probably due to bacteria, which produces a stain in the hide wherever blood remains. This statement is made by some one who is supposed to know, and I would like to ask Mr. Yocum's opinion about it. Does the presence of the blood in parts of the hide make a salt stain where the blood is?

MR. YOCUM:—I never have done any special work on the subject. I have always taken Dr. Fiebing's statement that the presence of blood containing iron would occasion salt stains if it was not properly washed out, and yet the character of a salt stain is such that it would hardly seem to be caused entirely by one thing. If hides are put in bundles and piled up and left for three months or so, there will be salt stains across the fold of the bundle. I have read some of the articles you speak of in which they say it is bacterial, a change of some of the nitrogenous material into pigments of some sort, but I have also experienced this, that where hides are unhaired and then go into acid solutions, they do not retain some of the salt stains. It is only where there is an opportunity for the fixation of some compound that is existing there. It would be natural to conclude that the iron in the blood had considerable influence on it rather than any bacteriological action, because if a given hide is put into an acid solution and shows no salt stain, but when put into some solution that is not so acid does show salt stain, it is fair to conclude that the acid had something to do with its

Digitized by Google

removal. It could not have anything to do with the bacteriological action; it would be a chemical action.

MR. LOCKWOOD:—I think the procession of events during a good many years has sort of automatically thrown some light on this salt stain question, and what I shall say will be in line with what Mr. Yocum has said. Probably a number of you remember that perhaps a little less than twenty years ago there were apparently more hides than the tanners could use and the packers frequently carried their long-haired winter hides through the summer and began to take off long-haired hides again with all the previous winter's hides on hand. The salt stain question was discussed 50 per cent. more then than it is to-day. It was a great evil, all the tanners were complaining about it and the trade papers were full of talk about salt stains, and of course there were elaborate theories as to what caused the salt stains just as you are expounding theories to-day. I did not understand them then and don't to-day, as I am not a chemist. But as hides began to get scarcer and as packers began to do what they had never done before, sell them in advance of the kill, so that they did not have to carry hides any great length of time, the salt stain business began to fade away.

MR. YOCUM:—As Mr. Lockwood has said, there is absolutely no question about the element of time entering into the question of salt stains, but time itself does not explain why we have salt stains. We certainly do have more salt stains on hides that have been packed a long time or hides that have been repacked than we do on fresh hides, yet the time element itself will not occasion salt stains. We have to go a little further back than that to determine what the action is. Personally I am disposed to credit the theory, as I said before, that it is caused by the iron in the hæmoglobin of the blood under certain conditions of moisture, time and salt.

MR. MORRISON:—While we know that time has something to do with salt stains, it is evidently a fact that we get more salt stains from hides that have been salted with dirty salt than we do from a clean, fresh salt, regardless of time, and I have found it that way in my experience; but I have opened bundles of hides where the salt stains along the fold were so heavy it looked like

Digitized by Google

a heavy rust. It goes to show that time has something to do with it, but dirty salt has a good deal to do with it too.

MR. YOCUM:—I think Mr. Morrison is quite correct in his statement, because just as I said here a few minutes ago, there is a certain brokerage house that has advised the packing of hides with clean crystallized salt and they claim that they have not had anything like the prevalence of salt stains that they would if they had used the ordinary mine salt.

MR. DESMOND:—I should think that with the conditions ruling in the hide market now, the question of time would be decided, because there are no hides left in pack too long; but aside from that question I do want to say that as a tanner I appreciate very much that the chemists are taking up this question of raw material, which forms 70 or 75 per cent. of the largest bill the tanners have, and probably the most uncertain thing that the tanners have and have had for twenty-five years.

MR. MORRISON:—We still find lots of salt stains on the hides which come from the packers to-day.

MR. GRIFFITH:—In spite of the fact that they are not liable to lie in the cellars at all now?

MR. YOCUM:—Mr. Griffith, they have got to lie in the cellars. No broker would take up hides unless they had been in the cellars at least four weeks.

MR. DESMOND:—I believe Mr. Morrison made the statement that some of the packers' hides have salt stains to-day, but it is also true that here and there there are lots of packer hides that have been in the salt for six to eight months, and it is possible that it is those particular lots which show the salt stains.

MR. MORRISON:—I admit that, but on the later months' take-off, that have not been lying in the beds longer than the rules call for, there will be salt stains. I just mention this to show that it is not the lying in the bed so long that creates all the salt stains, but that we get salt stains from hides that are not laid a long time in the beds. I admit there are lots of packer hides to-day that have been in the packers' hands longer than thirty days.

MR. YOCUM:—I might say as an explanation of the basis of some of my opinions, that in the last year or so I have had oppor-

Digitized by Google

tunity to see the working of unsalted hides to the extent of probably 20,000 or 25,000 hides, and I have yet to see a hide that has a salt stain on it from stock that had never been in salt.

MR. LOCKWOOD:—To really understand this matter it is well to know that the length of time it takes to cure hides is the length of time it takes to make a pack. It is a merchantable proposition and not a mere proposition of curing hides; so that when the packers are killing one kind of cattle, and so on, they make up the different packs, and of course a pack must be completed and it may take a considerably longer time to complete a pack of a given selection than to cure the first hides that go into that pack. Therefore, while they are selling them as quickly as it is possible, yet inevitably some hides must remain in the pack in salt very much longer than the time necessary to cure them; so that there are always hides lying in salt under every condition,—some hides,—and a considerable number of hides are in salt much longer than the time necessary to cure them.

MR. DESMOND:—We had more hides than we knew what to do with in 1908, and during the warm weather we were compelled to resalt some of them, and of course we were very careful about the salt used. It was the best rock salt, and to my knowledge there was not a hide in the lot that was salt stained, and I know we carried some of them along six or eight months, and it is quite possible that if the investigation was carried back into the packer's hide cellar and into the dealer's hide cellar, a good deal of the source of the salt stain would be discovered there.

MR. MORRISON:—I am positive of it. I have seen hides that have been in salt for six months and did not show any salt stain. They could all be worked into fair leather. Then again hides from the last month's take-off may show salt stains. If the hide is traced back to the hide cellar you will find a great deal of the trouble.

MR. DESMOND:—May I interrupt with the hope that the chemists will keep on with this investigation, because from the tanners' standpoint it is very desirable.

Digitized by Google

MR. GRIFFITH:—It is encouraging to the chemists to have a practical tanner come here and tell them that. What the chemists really need is more encouragement in that manner from the tanner, and I know that chemists are only too glad to coöperate with tanners in solving their practical problems, but a chemist who is confined to a laboratory and has no chance to go into the tannery cannot be expected to explain something that he has not had an opportunity of observing. Now in the matter of the trouble with salt stains, there is one thing you have to follow right down to the root of the evil, and the root of the evil is in my opinion the salt cellar. I once had an opportunity of tracing a difficulty of that kind which occurred in the tannery, and we traced the difficulty to the cellar where the skins were salted, and we discovered that they were using salt that had been used over and over again. When we had established the cause we could remedy it, and we did succeed in remedying it. What the chemist has to ascertain is the cause, and it is not always easy to study the cause from observing the effect, so that I appreciate personally your remarks in regard to the encouragement of chemists along practical lines.

MR. HURT:—While it is not possible to trace the cause of salt stains into the packer's cellar, at the same time the tanner gets a hide and he has the salt that the packer has put on it. If he can get his chemist to determine the iron in the salt he could probably determine that.

MR. GRIFFITH:—That is not always easily done, Mr. Hurt, because the conditions in the salt cellar will really throw more light on it than the examination of the salt, because you see there isn't very much salt left on a hide; it is shaken off, and the trouble has already penetrated beyond the immediate observation of the observer. Your suggestion, however, is of course a thing one would logically do in making any investigation. Take the case I have reference to in my own experience; there was no salt to work on at all. It involved a very large claim, and we had to find out the exact conditions under which those hides were cured.

MR. CLAFLIN:—Would it not be in order to suggest to the council that they appoint a committee to investigate the question

Digitized by Google

of salt stains? There are members of the association who spend much of their time wandering up and down the country, who are also chemists, and they have a good opportunity to observe. I have always understood that salt stains were caused by iron in the form of ferric chloride, that could come from the iron in the salt or the iron in the blood, but it is a matter easy of ascertainment. There has been some work done abroad on this, but I think we would make better progress if we had a committee appointed to look into it and make some sort of a report on it. If it is not too far from the purpose of the society, I would suggest that it be done.

MR. YOCUM:—In connection with Mr. Claflin's remarks, I think it would be very wise to have some committee appointed to investigate the causes of salt stains, but that committee might at the same time try to establish some uniform method of selection of hides and the treatment of hides in the packers' cellars.

MR. REED:—Can you do it?

MR. YOCUM:—No. We can try.

MR. GRIFFITH:—I know the council would be glad to give the greatest consideration to Mr. Claflin's suggestion, but I do not know just along what lines they could proceed. As. Mr. Yocum says, and I believe he speaks seriously, it is a very difficult matter to try to classify the selection of hides. I do not believe anybody can do it.

MR. CLAFLIN:—I do not think it is a question of classifying the selection. We know there have been statements made in very many representative journals that salt stains are caused by mold growths or are of bacteriological origin; then there is the other statement that they are occasioned by the iron in the salt or that comes from the blood. If we knew what was the cause—and it does represent a great monetary loss—it certainly is possible that something could be done to remedy it. No loss is so slight that if its remedy costs less than its persistence it will not be remedied, and I think it just as well to find out something in reference to what we are talking about.

MR. LOVELAND:—I would like to say that I have tested a great number of salt stains and I have never found a salt stain on a piece of leather that would not give a test for iron. Place

Digitized by Google

a piece of filter-paper, moistened with hot water on the stain, wet that with hydrochloric acid and it will respond to any test for iron.

MR. DESMOND:—I am inclined perhaps from a tanner's standpoint to look at the matter of salt stains as rather a particular part of a general proposition. What I was pleased about, and am pleased about, is that the chemists as an association are going to help the tanner in a general way on improving, as I say, the biggest part of his raw material, and in seconding Mr. Claflin's suggestion I would only suggest that it be made broader instead of being so specific on the matter of salt stains.

On motion of Mr. Claflin, it was resolved that this meeting consider it advisable that the Council appoint a committee to investigate the salting and curing of hides, with special reference to salt stains.

THE TANNING PROPERTIES OF WASTE SULPHITE CELLULOSE LIQUORS.[1]

By Alan A. Claflin.

From the time when Humphrey Davy investigated the chemistry of the Tanning Process at the request of the Royal Society to the present day our fund of exact knowledge concerning that chemistry has not greatly increased. On the other hand we can scarcely over-estimate the advance that has been made in the scientific technique of the art. It is paradoxical to say that we do not know what we are doing any better than we did a hundred years ago, but are doing it much better, yet that is exactly the case with leather making. One reason for this condition is that leather is not a single definite product but a general title for a class of products which have only this in common, that they are made from an animal skin. Thus we have leathers which there is every reason to believe are simply raw skins preserved by mechanical lubricants, and leathers which are of very stable although variable chemical combination, and all stages in between. The attempt has been made perhaps successfully to limit in a chemical sense the term leather to those compounds of tanning

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec., 1911.

Digitized by Google

material and the hides which are reasonably resistant to the swelling action of dilute acetic acid and to the solvent action of hot water. Unfortunately there is at the present time in this country an objection to these qualifying terms, particularly in definition. Reasonable restraint of trade means one thing to the seller and another to the buyer. So in calling a compound a tanning extract or leather-making material while we may say one product definitely is and another definitely is not, there will be a borderland on which may repose various materials which will be classed according to the point of view. To this class belong those products offered to the tanning trade abroad as Fichtenholz Extracte and in this country under equally felicitous names, which are made from the more or less purified waste liquors of the sulphite cellulose process.

The way these products broke into the tanning trade is interesting. It was by the back door so to speak. About seventeen or eighteen years ago these lyes were a source of considerable nuisance, for that matter they still are in many places, but at the time referred to in Germany prizes were offered by the pulp makers association for their utilization. I do not know whether any of the prizes were actually awarded, but one of the results of the agitation was a product called ligno-rosin which was offered to the dyeing industry as a substitute for lactic acid as a reducing agent for the bichromates. Its variable composition and the fact that it deposited a gummy insoluble mass militated against its use for dyeing to any great extent, but as it had been offered as a substitute for lactic acid in one industry nothing was more natural than that it should be offered also in the tanning industry where lactic acid was then beginning to find its widest use. Here it was soon developed that while it very imperfectly performed the functions of lactic acid, according to the hide powder method of analysis, it did show large percentages of tannin. It was at once claimed and is still contended that this content of tannin is more apparent than real, because by the Lowenthal volumetric method results only about one-sixth as high are obtained. The beginning, however, was made. First offered commercially only as an adulterant, or extender, blend or whatever is the preferable item in mixture with chestnut

Digitized by Google

extracts, these sulphite cellulose liquors soon became of sufficient importance to be sold for their own virtues. In this country the development was somewhat later and perhaps not exactly parallel, because the use first developed for American sulphite lyes was as a glutinous material, *e. g.*, for core binding in iron foundry practice, and then this glutinous body was suggested as a substitute for glucose and grape sugar as a loading material for sole leather. It soon developed, however, that it had a power of combining with hide substance far beyond that of glucose. This is about the state of the industry to-day. One side contends that these extracts simply have a loading value and the other that there is a true tanning value. Eitner in a recent article holds to the former view and holds that any tanning action is due to the presence of zinc sulphate. That this view is erroneous cumulative testimony is now gathering in this country. In the first place in American extracts there is no zinc sulphate present, and the results in tanning are greatly superior to anything Eitner reports. Indeed it seems to be a question of how the waste liquors are treated and how much purified and if sufficiently purified and properly treated there is to my mind little doubt but that the tanning properties of these liquors will be found to be far greater than the most sanguine of us now anticipate. The investigation of this subject is now being undertaken in our laboratory and it is to be hoped that before we have another annual meeting that certain positive results will be established.

DISCUSSION.

MR. PIERSON:—We are interested in sulphite cellulose extracts to the extent that we are making several combination extracts into which this extract enters as a part. In selling the extract of course we would be putting our heads into a noose if we did not say that the extract we were offering was a combination of sulphite cellulose extracts and other, what we call, active tannins, but we have been very much up against it on the question of analyses from different chemists agreeing, and if the tanner buying the extract happens to pick out the man who finds a high non-tannin content of course he considers that his man is right. To illustrate: We shipped a tank to a user and he drew

Digitized by Google

his sample at the tannery and sent it to his chemist whose findings were 23 per cent. tans and 25 per cent., I think, non-tans. Three other chemists to whom we sent samples drawn at the factory at the time the car was shipped found from 25 to 26½ per cent. tans, and a corresponding amount of non-tans to make up the total solids. We should like very much to have some method established that would make it possible for the chemists' findings to agree on combination extracts containing waste cellulose liquor. I just offer that as something that could be discussed here by men who do the work.

MR. LOVELAND:—Was the sample drawn at the tannery also analyzed by the several different chemists?

MR. PIERSON:—I ought to have stated that when this discrepancy appeared we asked for a portion of the same sample that was sent to the chemist who found the low tans and fortunately the tanner had it, and so we were able to get reports on the identical sample. Three chemists found what we guaranteed in tannin and the fourth found less.

MR. CLAFLIN:—I wish to say for the benefit of the chemists that in the experience we have had in selling these sulphite cellulose liquors we have never had any trouble at all in getting concordant results from the chemists on analyses sent out, and we have sent to at least half a dozen chemists, and I think the results on tannin have been fully as concordant as we ever get on chestnut extract and more concordant than we ever get on quebracho.

MR. OBERFELL:—Isn't it a fact that we only have trouble on perhaps mangrove and these sulphite liquors or extracts, in getting the non-tannin filtrate which does not show a precipitate with gelatine? I have never heard of it being questioned in any other one.

MR. REED:—I would include also pure oak bark and pure hemlock bark extracts. We have the same trouble with them.

MR SMALL:—Also certain makes of chestnut wood extract.

MR. VEITCH:—I have had the same trouble with quebracho. I think that is a question of how thoroughly the hide powder is washed,—its acidity.

MR. OBERFELL:—You mean its original acidity?

Digitized by Google

MR. VEITCH:—Its acidity after it is ready to use. That is when it counts; not before; and the time, and quantity of hide powder. There are a number of different factors that enter into it.

MR. OBERFELL:—These things did not seem to develop when we were making up our methods. The methods were based on a great deal of work,—collaborative work which agreed. The amounts were prescribed at that time.

MR. REED:—If I recall rightly, the hide powder we used to have was more acid than it is now. Isn't that so, Mr. Alsop?

MR. ALSOP:—Years ago the hide used to be more acid.

MR. REED:—I think that accounts for it.

MR. SMALL:—I think also there has been a change in the method of manufacture of extract which accounts for some of this present trouble.

MR. VEITCH:—Further, I think that some of these things were observed and discussed, but they were not considered of sufficient magnitude and so few had had experience with them that they did not affect the accuracy of the method materially.

MR. REED:—Reverting again to the acidity of the hide powder, it seems to me much of this could be overcome if we did have a little more acid hide powder. I don't know whether the association wishes to consider it or not. I think it would be a good thing to do so.

MR. DICKERSON:—Speaking from our own experience, we have found the same thing as Mr. Pierson, and speaking for myself personally, I feel that some exact method ought to be established by the association to cover that very point, and I want to ask Mr. Reed if he has had any experience in determining whether the degree of extraction of any tanning material will not show up a variant degree in the coloration of the non-tannin filtrate; in other words, the more drastic the extraction the more high the coloration of any material.

MR. REED:—No; I do not think that necessarily follows at all.

MR. DICKERSON:—What effect does the difference of the acidity of the solution make? Do you get the same results in acidifying the solution as in acidifying the hide powder?

MR. REED:—You do not always get exactly the same results.

Digitized by Google

MR. LOVELAND:—Doesn't the proportion of non-tannins to tannin in shaking with hide powder have quite an effect? For instance, if you take a fresh mangrove bark and leach it and take a spent mangrove bark and leach it, the proportion of non-tans in the mangrove are different, and I find it very difficult to clear up a spent mangrove bark non-tan, whereas a fresh mangrove bark non-tan is very readily cleared up.

MR. REED:—I would say in regard to the analysis of sulphite cellulose extract that I myself, working on the same extract, have had difficulty in getting good duplicates. I don't know why it is. It seems that there must be some condition there of absorption that is not uniform. I can't discover what the cause of it is exactly. If you vary the amount of extract taken for the original solution you will very materially, in the case of sulphite cellulose extract, vary the non-tannin content more than you will in ordinary tanning extracts. Mr. Yocum and Mr. Faust have published an interesting article on the question of the blends of sulphite cellulose extracts with other tanning extracts, and I have done some work along those lines too. I think the explanation of their results is very simple. The question is one of selective absorption. I do not know whether it follows necessarily that the action will be the same in the tannery. For instance, consider the analysis of a mixture of chestnut extract and a sulphite cellulose extract. My view of the matter is this, that the hide powder has a selective absorption for the chestnut extract tannin. It takes it out and becomes partly tanned. Partly tanned hide powder has not the absorptive power for the sulphite extract that the untanned hide powder has; therefore there is less absorption of tannin, or whatever it is, from it, and the result is that you get in a mixture of the two a higher non-tan than the theoretical value of the two done separately.

MR. FAUST:—Selective absorption does not explain the increase in insolubles we found upon mixing sulphite extract with other tanning extracts. Do you know anything about that?

MR. REED:—In my work I did not get such results. Perhaps we were working with a different sulphite cellulose extract, which may account for it, but I got lower insolubles on the

Digitized by Google

analysis of the mixture than I did calculating the average of the two done separately.

MR. FAUST:—I have used two different kinds of sulphite cellulose liquors and I have obtained entirely different results.

MR. OBERFELL:—This discussion has been up for three years. We have never done anything about it. Mr. Alsop raised it two years ago here in Washington, as to whether the chemist should use the official amount of hide powder or whether he should detannize until he gets no precipitate. It seems to me that we ought to standardize this somehow. Give the chemist a right to detannize all solutions until he gets no precipitate with gelatine or follow the official method to the letter, the prescribed strength of solution and the prescribed amount of hide powder, and then if he obtains a precipitate containing tanno-gelatine, he should make such a note on his report. Then they would know where they are standing in comparing various analyses.

MR. REED:—As a matter of fact would not the results be more comparable between chemists if we could get a clear non-tannin filtrate?

MR. OBERFELL:—My experience has only gone to this point: I would use the official amount of hide powder and the official strength of solution, and if I got a precipitate, and if I knew it was one of these materials about which there was some question, I would state on the report that the non-tannin filtrate did give a precipitate with gelatine when I had used the official method. I would not think it fair to go ahead and use more hide powder if the solution was of proper strength, so that I have no line of comparison as to what would be the result if you completely detannized in all cases.

MR. REED:—Doesn't the official method say the non-tannin filtrate shall give no precipitate with gelatine?

MR. VEITCH:—It does, but it does not provide for what you must do if it does give a precipitate.

MR. REED:—That is the point.

MR. DELANEY:—The official method says you shall take from 0.35 to 0.45 gram of tannin. There is a fairly wide field in there provided the amount of the hide powder is varied. The regular amount of hide powder for 0.35 gram will not be enough for

Digitized by Google

0.45 gram and vice versa. Mr. Rhoads suggested that next year there should be some, you might say, official analyses made of one of the extracts that everyone is interested in, say chestnut wood liquor, and it should be run through under the supervision of the people interested in that sort of work. Why would it not be a good thing to have one or two analyses run through under the conditions used in the laboratory and see how they differ from those used in our own laboratories? The difference is probably in some of the smaller details.

MR. VEITCH:—I think we have all had this difficulty, and while I have never been engaged in any commercial work on the matter, I would say that I have tried to meet it in work I have done. I have either shaken longer or let it stand longer, which removed the excess of tannin, or I have added a drop or two of dilute acetic acid, which also removes it, or another batch of hide powder would give me clear non-tannin filtrates. The official method won't cover all these conditions.

MR. FAUST:—I thought we were going to rewrite the official methods. On the one hand you follow the official method and can't get satisfactory results; or you deviate from the official method a little and you are all right. Now I think if the official method were rewritten with attention to that one thing we could get over it. That is, put a clause in providing that the non-tannin filtrate should be clear and if it is not clear we should use whatever we need to use to make it clear.

MR. HOPPENSTEDT:—It seems to me it is far better to let the filtrate part go. Leave out the gelatine salt test. We all know that we are using far more hide than is necessary to detannize, and if we have substances in there that won't combine with that hide it is better to leave them alone. It seems to me it would be much better to leave the method as it is, using the stated amount of hide, and then if the filtrate does contain tannin we can make a note to that effect, but not make it compulsory that the filtrate shall not give a precipitate with gelatine salt.

MR. DELANEY:—I would say in reply to that, that if you use the ordinary amount of hide powder for 0.35 gram tannin, you will not get the same results that you will from 0.45 gram.

Digitized by Google

MR. REED:—I believe a wrong impression has been left, because those limits were fixed from a great deal of collaborative work and it was found that the amount of hide powder prescribed was sufficient for the amount of tannin contained between those two limits.

MR. VEITCH:—It seems to me we are not having much greater difficulties than they have in other lines of articles sold on analyses. The same difficulty is met in the manufacture of fertilizers, and in fact everything where a very high percentage material is concerned; and it is not unusual to get two chemists differing 2 per cent. in other lines of work. Now about Mr. Hoppenstedt's remark about the quantity of hide: Years ago I did something on that, and there isn't any doubt that by shaking long enough with half as much hide the tannin can be removed. There are a number of indefinite things on which we will have to do a lot of research work, but we had better go slow in changing the method until we have absolutely definite data.

MR. HOPPENSTEDT:—It seems to me that the point is not kept in sight that the precipitate we get after using the stipulated amount of hide is not tannin.

MR. VEITCH:—Of course not.

MR. HOPPENSTEDT:—Well, why worry about a substance in there that is not tannin at all? And it only comes up in such extracts as sulphite cellulose.

MR. VEITCH:—No; it comes up in all sorts.

MR. HOPPENSTEDT:—I have had a good many filtrates from oak extract that were not clear, but they never gave a precipitate with gelatine salt. I doubt whether there is any tannin left in them.

MR. DICKERSON:—The official method does not state whether you are examining for tannic acid or what it is. It is a question of determining the total amount of material there that is absorbable by hide substance. Now we know—and it has been brought out by the different members in their investigations—that acidifying will take care of the trouble, or longer shaking or standing will do it. Now it is for the association to say what is to be decided upon to take care of that point.

Digitized by Google

MR. LOVELAND:—I would like to ask a question to bring the matter under discussion: Whether the proportion of non-tans and tannin have a bearing on the matter? Now we take a sulphite extract and the non-tannins are about 25 per cent and the tannin 25 per cent. When we weigh that to get between 0.35 and 0.45 gram tannin we weigh out a large amount. In the case of new and spent mangrove bark it is the same thing, and in one case of chestnut extract where the character of that extract has changed within the last year I find considerable trouble in checking their chemist's results. The extract has changed from about 14 per cent. non-tans to 18 per cent. non-tans, and I have trouble in getting clear filtrates. Doesn't the ratio between non-tans and tannin have a bearing on the clearness of the filtrate?

MR. OBERFELL:—I think it would be a good thing to have the council take this up and consider the subject and make some suggestion for changing the official method, whatever is necessary. Clear it up once for all.

MR. REED:—There is one suggestion I would make when the council takes it up. I think it is perfectly possible to limit the amount of hide closer than we are doing it now. I think 13 to 14 grams could be changed to closer limits. I also think it is possible to alter the proportion of tannin. I think we can limit that closer. I think if we make those refinements we will get closer agreement between different analysts.

MR. CLAFLIN:—I would like to suggest before the council take up this method of modifying the method of analysis that they gather what information they can as to what is the average difference of result between different chemists. Now Mr. Dickerson and I are speaking from the same figures, but from a different point of view. I consider the results were very satisfactory, considering that the method of tannin analysis is a purely empirical one. The results that chemists get on tannin analysis compare favorably with the results we get on the analysis of babbit metal. I think the biggest difference in result we get from two chemists is approaching 2 per cent., say 1.7 per cent.; that is, one will be 31 per cent. and the other will be 29 per cent.

MR. VEITCH:—This is the same view of the matter that I took about four years ago at the Chicago meeting, and I really think

Digitized by Google

Mr. Claflin is right about it. We are getting as good results as we can hope to get with the methods that we have on materials as high in the constituent to be determined. I think that when two or three chemists differ no more than 1 per cent. in tannin on a 25 per cent. extract, that is good work.

MR. HALEY:—The discussion here seems to point to changing the official method for the determination of tannin in vegetable tanning materials to cover a new class of materials that has arisen. When the present method was adopted it covered the analysis of all the tanning materials that were known at the time of its adoption. If new materials have arisen since then, calling for a new method, let us devise a new method to test those materials by and leave the present method as it is, covering the materials that it is supposed to analyze. I had hoped that the committee that was appointed on the sulphite cellulose extracts would have a report, devising a method covering the analysis of this class of materials. I was a member of that committee but I never received any official notification from the chairman of the committee that any work was to be done on the subject.

MR. REED:—I do not understand that the discussion has led to the conclusions that Mr. Haley seems to think it has. It is not to change the method; it is to be more specific in the method.

MR. PIERSON:—If I have properly understood what has been said, the question does not hinge on waste sulphite cellulose liquors; it is a question of discrepancies. I think a number of you have said you have found discrepancies not only in that but in chestnut and mangrove extracts, and we are not any more interested, speaking for my concern, in sulphite cellulose than any of the others; but we have been up against it on combinations that contain sulphite cellulose liquors. I do not think the change is asked to favor that class of liquors particularly, or that class of extracts.

MR. DICKERSON:—Speaking personally, I don't want the association to think that those interested in the manufacture of waste sulphite cellulose extracts are looking for any special favors to take care of their product at all. It is simply that we want some rules laid down in the official method which will take care of

Digitized by Google

this matter properly so that we can get comparable results from different sources, from different chemists; that's all.

MR. DELANEY:—Don't you think that subject of the discrepancy between different chemists could be well settled by getting samples of extracts from various sources and sending them out to various members who would be willing to make analyses and then see what the discrepancies were, if any, and decide it later?

MR. ALSOP:—The present method of tannin analysis is the best one we have been able to devise for the analysis of vegetable tanning materials containing tannin, and I would be very loath to see the method changed in any respect on account of sulphite extract. Any slight modification in our method which would bring about the results to be desired in the analysis of that material might lead to much greater discrepancies in the analysis of ordinary materials.

MR. YOCUM:—I don't think Mr. Alsop means to say that a modification of our present methods, that is, a more complete distinction of what our methods are, would lead to greater discrepancies.

MR. ALSOP:—One thing I might refer to would be the addition of acetic acid to the solution. I think that is very undesirable.

LIME AND ITS PREPARATION.[1]

By Louis T. Roenitz.

In approaching the subject, as it applies to the leather business, I shall try to do so more from the lime man's standpoint than from that of the leather man. During the past year or so I have been associated with men who have had much experience in the manufacture and distribution of lime. This has given me an excellent chance to gather information about the product itself, and to get a line on the relative value of the product of one locality, as compared to that from some other, especially as regards the leather business, and so I am going to try to pass some of this information along to you this afternoon in the hope that what I have to say will be at least interesting and may be

[1] Read at the A. L. C. A. Convention, Washington, D. C., Dec., 1911.

Digitized by Google

instructive. My data come from a territory bounded by the Lakes, Allegheny Mountains and the Ohio and Mississippi Rivers, but much of what I have to say will apply from coast to coast.

To one who becomes interested in lime, it appears strange that there is so little printed information on the subject. I doubt whether there is another product in the industrial world so ancient of origin and so widely used, upon which so few authentic data are available. I presume it is because of its low value as a commodity that the study of lime was pushed aside for the apparently larger and seemingly more important articles. I believe you, as technical leathermen, will agree with me that the subject of lime and the process of liming has not come in for the same sharp scrutiny and study as other materials and points in your work. In fact, it is only recently that it has been generally conceded that the lime bath is one of the crucial stages in the art of leather making; and even where, in individual cases, the importance of proper liming was recognized, the old fallacy that "lime was lime and all lime was alike" often held sway. There has been a wonderful change in this respect during the last two years. Now, generally speaking, the same fine discrimination which has been long applied to other chemical requirements of the tanner is exercised in the selection of his lime.

That something cannot be made out of nothing is as true in the lime business as it is in the leather business, the lumber business or the world in general. If you are to turn out a finished product of quality you must have first-class raw materials to start with. There are two main classes of limestone, dolomitic and high carbonate, the first analyzing when pure, 54 per cent. calcium carbonate and 44 per cent. magnesium carbonate. The high carbonate runs when pure, between 98 and 99 per cent. calcium carbonate. While the dolomitic limes seem to be on a parity with the high calcium products in building operations, they have no place in industrial operations where only the calcium content of the lime is of any service. This point has been overlooked until recently, by a great many tanneries, and even yet there are some who use limes of only 50 per cent. efficiency.

A brief, superficial glance at the limestone deposits of the

Digitized by Google

Northwestern quarter of the United States, as set forth in the different State Geological Surveys, might not be amiss at this point. East of the Allegheny Mountains we find mostly high carbonate stone. This is particularly true of Maine, Massachusetts, New York and Virginia. From the Allegheny Mountains west is a wide belt swinging around the Great Lakes, taking in Ohio and the northern halves of Indiana and Illinois and the state of Wisconsin, where we find the dolomite. South of this strip the stone gradually changes and runs more nearly into the high carbonate as it approaches the Ohio River, while south of it, for instance in Tennessee, some excellent stone occurs. Going west we do not find this gradual change, but on the Mississippi River some of the best and purest deposits of high carbonate stone in the country are found, especially in Missouri.

The methods of manufacturing lime should be of interest to you as consumers, especially the methods of quarrying the rock. You are all familiar with the general method of open quarrying, that is, where the rock is drilled from top to bottom and all shot down in a pile. This method has recently been improved on by some operators who tunnel for their stone, going straight into the hillside with halls and rooms much as in a drift coal mine. Of course, this is a little more expensive, but it eliminates the impossible task of having to separate the good from the bad, as is the case where the good stone, the top rock and stripping are all shot down into one intimate mass. The advantage is evident, for it insures an absolutely pure and uniform stone with which to work.

The next step, from stone to quick-lime, is an ancient and well known process with which you are all familiar. The hydration of lime as it is done on a commercial scale, is, however, a comparatively modern accomplishment and therefore may be of some interest to you. As one lime man has expressed it, "it is a forward step in a backward business." Divested of technical terms, hydrated lime is freshly burned quick-lime scientifically slaked to a dry powder. You understand, better than I do probably, just what happens when lime and water unite; how the lime unites with 24 per cent. of water by weight in a chemical reaction. Now the lime man has essayed to perform this service

Digitized by Google

for you and has installed the necessary machinery with which to do this work. The quick-lime as it comes from the kiln is put through a crusher, which reduces it to a size ranging from that of a pea down to dust. In this form it is positively fed into the hydrator. The water scientifically calculated as to amount, and automatically regulated as to application, is admitted in the form of a spray, as the mass is being continually mixed and passed along by the conveyor paddles. This takes place in a series of steel cylinders one above the other with openings at the end leading into the next one. Through these the mixture drops after passing through a cylinder. The whole machine is surcharged with steam generated by the operation, and thus, every particle of the lime, no matter how small, is combined with the water. From the machine it passes over screens where it is bolted, or is mechanically separated from the tailings or waste particles by air.

And does it not seem that this machine which is the result of careful experimentation can carry out this reaction more accurately, more satisfactorily than the common laborer with his hoe and tub? There is probably no clear conception of the immense amount of lime that is ruined (*burnt,* the lime man would say) in slaking. You, as chemists, should be able to appreciate this. You know what extreme care you take in carrying out many chemical reactions, but here is one, subject to the very same exacting laws and principles as the others, left to the laborer.

Hydrated lime comes in the form of an impalpable powder, out of which, as we have seen above, all free impurities have been screened. It is generally packed in 40 pound patent self-sealing paper bags. In this form it is much more easily handled and stored than quick-lime and eliminates all risk of fire. As you know, all insurance companies take the storage of quick-lime into consideration when computing rates and setting the limits of their policies on tanneries. This is, however, a minor consideration. The real advantages which, it appears to me, should recommend it most strongly to the leather man are its uniformity and stability. It would be a great relief to the tanner if the ever present annoyance of loss from air slaking and the resulting uncertainty which it causes in their work were elimi-

Digitized by Google

nated, and that is just what hydrated lime will do for him. You are familiar with the waste too often left in the slaking tub in the form of stone and chert, even when using a good lump lime. Did you ever stop to think that you bought this waste material, paid freight on it, paid labor to handle it into your work and out again, besides the annoyance you were put to by its presence? Not only is this waste very expensive, but the grain of the skins is often scratched by the hard gritty particles coming in contact with them, reducing the grade and therefore the value of the finished stock.

Lime in the hydrated form is far more stable than the quick-lime in any form. As a technical man you would expect this, for I am told that, generally speaking, the hydroxide is a more stable compound than the oxide. A law of physics as well as one of chemistry enters, however. The hydrate comes in minute particles and these, on account of their infinitesimal size, can lie so close together that the penetration of carbonic acid gas is rendered well nigh impossible, at least to any considerable depth. So, when it becomes necessary to keep it in storage some time, say for a year, a thin film next to the paper carbonates, which acts as a protection to the rest and thus, as a whole, it keeps indefinitely. The total loss under normal conditions of a well hydrated lime in storage for a year does not exceed 5 or 10 per cent.

The use of hydrated lime in tanning operations decreases the item of labor cost. I believe the product in this form and packed in this manner affords an ease in handling both into and out of storage, as well as into and out of the vats, that results in a considerable saving. The task of slaking is reduced to one of simply mixing, while the waste or sludge is reduced to the minimum, and the labor necessary for its disposal correspondingly decreased. The only seeming disadvantage or objection which the writer has ever heard expressed, is that owing to the absence of the heat generated by the slaking of quick-lime the proper combination of arsenic and the lime does not take place. This objection is more seeming than real and was easy of solution. Dr. Louis E. Levi in an article on this subject outlining a series of tests which he had conducted found that the use of a water of about 85° C.

Digitized by Google

solved the problem and gave excellent results. This article can be found in the May 7, 1911, issue of *Hide and Leather*.

In conclusion I do not think it is too much to say that the introduction of hydrated lime into the beam house marks a forward step in the evolution of a more accurate and more scientific process in a department where crude methods and crude materials have too long held sway.

THE TANNINS.

Characteristic Reactions of Value for their Identification and Detection in Mixtures.

By A. W. Hoppenstedt.

(Second Paper.)

In order to avoid any misunderstanding, the author wishes to remark that all the tests given in the work take into consideration not only the tannins of the individual sections, but all the tannins which are being considered. A list of these follows:

Quebracho	Chestnut
Mangrove	Valonia
Gambier	Sumac
Cutch	Myrobalans
Hemlock	Divi-Divi
Chestnut Oak	Algarobilla

Sulphite-Cellulose

Mangrove.

Take 25 cc. of the tannin solution and add slowly while stirring, 25 cc. of a 1 per cent. solution of quinine hydrochloride. Then filter. Place 5 cc. of the clear filtrate in a test-tube, add 1 cc. of concentrated acetic acid and mix. Then add 2 cc. of acetone and mix again. Then add 5 cc. of ethyl acetate, mix thoroughly by shaking and then allow layers to separate. With mangrove the lower layer is colored a strong yellow-brown, whereas with all of the other tannins the layer is colorless.

The Author, Not Published Before.

This test is an excellent one for identifying mangrove and detecting it in mixtures.

Digitized by Google

Gambier.

Place 5 cc. of the tannin solution in a test-tube and add 5 cc. of alcohol. Mix. Then add 1 cc. of a 10 per cent. solution of potassium hydroxide and mix again. Then add 10 cc. of petroleum ether, mix by shaking and then allow layers to separate. The petroleum ether, forming the upper layer, assumes a strong green fluorescence.

DIETERICH, *Pharm. Central-Halle, N. F.*, 1896, 17, 855.

This reaction is not given by any of the other tannins and it forms a good test for identifying gambier and detecting it in mixtures.

Cutch.

Place 10 cc. of the tannin solution in a test-tube and add 10 cc. of ethyl acetate. Mix thoroughly by shaking gently and then allow layers to separate. Immerse part of a slip or shaving of any pine wood in the upper layer for one minute and then remove and allow wood to dry. When dry, dip the immersed part in and out of concentrated hydrochloric acid and then let stand for 15 minutes, after which note color. The part which has been immersed assumes a strong violet-red color.

H. R. PROCTER, Leather Industries Laboratory Book.

Modified by the Author, Not Published Before.

This reaction is very delicate but it is also given by gambier and slightly by hemlock, though not by any of the other tannins. It is therefore only applicable in the absence of gambier and hemlock.

Section B.

Green Blacks with Ferric Alum.

For Test See Above.

The tannins in this section give a green coloration.

Not Completely Precipitated by Formaldehyde and Hydrochloric Acid.

For Test See Above.

The tannins in this section give an intense blue ring at the junction of the liquids.

Digitized by Google

Tannins of This Section.

Hemlock[1]
Chestnut Oak

Hemlock.

Take 50 cc. of the tannin solution and add 10 grams of dry anhydrous calcium chloride C. P. Agitate until dissolved, then cool and filter. Place 5 cc. of the clear filtrate in a test-tube, add 1 cc. of concentrated acetic acid and mix. Then add 5 cc. of amyl acetate, mix thoroughly by shaking and then allow layers to separate. With hemlock the upper layer is colored a strong yellow-brown, whereas with all of the other tannins the layer is colorless.

THE AUTHOR, Not Published Before.

This test is an excellent one for identifying hemlock and detecting it in mixtures.

Chestnut Oak.

Place 25 cc. of the non-tannin filtrate, as obtained by the Official Method, in a 250 cc. beaker, add 1 cc. of strong ammonia and mix. Place the beaker on a piece of black paper and observe the appearance of the liquid from above. A strong blue fluorescence is given, especially around the edges.

H. R. PROCTER, Leather Industries Laboratory Book.

This reaction is not given by any of the other tannins and it forms an excellent test for identifying chestnut oak and detecting it in mixtures.

Part II.

Pyrogallol Tannins.

General Characteristics.

Not Precipitated by Bromine Water.

For Test See Above.

None of the pyrogallol tannins give a precipitate.

[1] It is evident that hemlock contains some pyrogallol tannin, though not very much. The blue ring given at the junction of the liquids is not so intense as with chestnut oak.

Digitized by Google

Slightly Precipitated by Formaldehyde and Hydrochloric Acid.

For Test See Above.

The pyrogallol tannins give only a slight precipitate.

Blue Blacks with Ferric Alum.

For Test See Above.

All the pyrogallol tannins give a blue coloration.

Section A.

Violet-Red with Sodium Bisulphite and Potassium Chromate.

Place in test-tube 1 cc. of the clear filtered tannin solution as obtained under determination of soluble solids and add 10 cc. of a 5 per cent. solution of sodium bisulphite. Mix thoroughly. Then add 1 cc. of a 2 per cent. solution of potassium chromate and mix again.

HUGH GARNER BENNETT,
Shoe and Leather Reporter, 1911, March 16.

The tannins in this section give an intense violet-red color which holds for some time. All the catechol tannins give only a slight greenish or greenish-brown color.

Tannins of This Section.

Chestnut
Valonia

ABSTRACTS.

The Analytical Examination of Bating. H. G. BENNETT. *Leather Trades Review,* Vol. 44, pp. 696, 972, Vol. 45, p. 28. Many so-called bates are chemical deliming agents, as coal-tar bates. salts of ammonia, weak acids, etc. A recently patented one is a solution of lactic anhydride in ammonium lactate. The author objects to calling these bates, as a true bate does more than deliming. When the word is confined to fermentive processes, there is still some ambiguity. Bates are made from a solution of glucose, with glue or other nitrogenous matter, to which cheese is added. The lactic ferment introduced by the cheese converts the glucose into lactic acid, which delimes the goods. These bates may also contain bacteria which dissolve some hide substance.

Fermenting infusions of dung are often called either "bates" or "puers." The writer follows Procter's distinction, calling infusions of dog-dung

Digitized by Google

puers and of hen or pigeon dung bates. The processes differ considerably in method and results. The author confines his discussion to bates thus defined. The process is empirical, being watched by an experienced foreman who by the "feel" and appearance of the goods determines the time of immersion, the quantity of dung, etc. In regard to chemical control, the writer quotes Procter's suggestions: (a) estimation of fats, (b) estimation of ammonia and amines by distillation with magnesia, (c) nitrogen (Kjeldahl), before and after, to determine loss. He thinks none of them yield results of much value, and has devised an empirical method of examination. The bate liquor is filtered and titrated with HCl, first with phenolphthalein and then with methyl orange, the former showing strong bases, and the latter the total alkalinity. Only one drop of each indicator should be used. Ten cc. of the bate liquors were used, and N/10 HCl. The method was first applied to the bating of ordinary "dressing" hides, the process occupying 5 days. The liquors were made from hen-dung, 2½ per cent. infusion, with 1 per cent. more when a second pack was put in; not strained nor filtered. Each pack was "washed through" an old bate liquor for some hours before being put into the new. The samples were taken in the morning, while the goods were being handled. The table gives cc. N/10 acid per 10 cc. liquor. The negative alkalinity in Example II was determined by N/10 KOH.

	Example I		Example II	
Day	Phenol-phthalein	Methyl orange	Phenol phthalein	Methyl orange
Thursday, goods in ...	——	2.3	—0.4	1.0
Friday	0.7	2.8	+0.2	1.45
Saturday	0.65	3.0	0.4	1.7
Sunday	——	——	——	——
Monday	0.5	3.2	0.35	2.0
Tuesday, goods out ..	0.5	3.6	0.35	2.3
Wednesday, goods in..	0.45	3.6	0.3	2.4
Thursday	0.85	3.8	1.0	2.5
Friday	0.8	3.9	——	——
Saturday	0.65	3.9	0.8	2.7
Sunday	——	——	——	——
Monday	0.45	3.9	——	——
Tuesday, goods out...	0.45	4.3	0.35	2.9
Wednesday	0.40	4.5	0.35	——

The alkalinity to phenolphthalein at first increases rather rapidly and then slowly decreases. When the second pack is passed through the same changes are observed. The author assumes that this is caused by lime from the hides diffusing out into the liquor and then being gradually neutralized by the acids produced by the fermentation of the bate. The diffusion at first is rather rapid and the bate is fermenting slowly, so the alkalinity at first increases, and presently reaches a maximum when the

Digitized by Google

rate of diffusion of the lime is equal to the rate of formation of the bate acids. As the fermentation increases, the alkalinity decreases. This gradual formation of the acids which neutralize the lime is paralleled by the gradual addition of the acid in chemical deliming. Toward the close of the process both the rate of diffusion of lime and the rate of formation of acid become very small. The alkalinity to methyl orange, which includes the other, continues to increase as long as the liquor is used, the rate of increase, at first rapid, becoming slower in the middle of the time and again increasing toward the end. Beside the alkalinity due to caustic lime, methyl orange shows the lime present as salts of acids too weak to affect methyl orange, and also organic bases, amines and ammonia. The fact that the alkalinity to methyl orange does not at first increase so rapidly as that shown by phenolphthalein seems to be due to the decrease of the organic bases during this period, due to their neutralization by the bate acids, which are strong enough to affect methyl orange. The rapid increase in the methyl orange alkalinity toward the end the author believes to be due to the formation of organic bases by the fermentation of the bate, after the acid fermentation has nearly ceased. This is the critical period of the bating process. To investigate this alkaline fermentation further would probably involve serious injury to the hides. The organic bases formed are probably other than ammonia, since they do not affect phenolphthalein at all. The author quotes J. T. Wood (this JOURNAL, V, 373) who says of the dog-dung puer, "The quantity of ammonia and volatile bases produced is very small, but non-volatile bases are produced in considerable quantity." The bating process seems to involve two types of ferments. The first produces the deliming acids and the second causes the solution of hide substance so as to separate the fibers and make the resulting leather pliable. The acid ferment seems to thrive best in a bate containing 14-28 parts CaO per 100,000, while the other (alkaline) ferment prefers a liquor having 8-14 parts. The author regards the second stage of bating as an incipient putrefaction. Another experiment was tried in which four packs were run through one liquor, each one remaining only over night. The results were similar in character to the others. L. B.

Red Mangrove Bark in Madagascar. CONSUL J. G. CARTER, Tamatave. *Consular Reports*, Vol. 15, No. 20. The value of "red mangrove" bark shipped from Madagascar since 1905 is shown in the following table:

Year	Metric tons	Price	Total value
1905	137	$16.44	$2,252
1906	1,408	24.26	34,736
1907	9,026	14.27	128,864
1908	3,754	12.31	46,214
1909	22,105	14.96	328,800
1910	36,181	14.56	527,833
1911 (six months) ..	24,441	14.04	343,200

Digitized by Google

The mangrove forests are on the northwest coast of the island, covering an area of approximately 220,000 acres, with an estimated average density of 1,000 trees per acre. The trees range from 6 to 12 inches in diameter and reach 100 feet in height. The estimates do not state what proportion of the mangrove trees are of species yielding tannin in paying quantities. Two species are cut, one (called by the natives *anabovahatra*) yielding much more tannin than the other (*tsitolony*). The botanical names are not given. The wood of the various kinds of mangrove is extensively used for building and other construction, and as fuel by the river steamers; also for charcoal. Only about 10 years are required for the trees to reach marketable size, so that the industry promises to be continuous if wisely managed. Concessions may be obtained from the Governor-General, the time limit for 5.000 hectares (13,500 acres) being 5 years; longer for larger concessions, but none above 20 years. The tax is 2 cents per year per hactare. The labor cost of the bark (dried) is from $5 to $6 per ton. Nearly the entire production goes to Hamburg in British and German ships. L. B.

Notes on Sewage Sludge and Its Disposal. Dr. J. Grossman. *Journal of the Society of Chemical Industry,* 31, 3-6, Jan., 1912. Disposal of sewage by water carriage is wasteful. The total waste for Great Britain is about $200,000,000 per year in manurial value. The recovery of this by chemical means would be a hopeless task, because of the great amount of liquid through which it is distributed. Another objection to present methods of disposal is danger to the public health. The dumping of sludge at sea has been shown to be dangerous because of contamination of oyster-beds, etc. In many English towns the settled sludge is filter-pressed and the cake dumped on land bought for the purpose. In some instances the cake is carted away by farmers for manure. Experiments on its manurial value show that it is not above $2.50 per ton for the dry matter contained. It is possible to gasify sludge cake, but the return is not sufficient to cover the cost. The writer has worked out a process for the distillation of sludge with superheated steam which recovers the grease, and by the removal of the fatty matters increases the availability of the residue as fertilizer, and at the same time sterilizes it so that it can be used with safety. L. B.

Tanning and Dressing Pigskins for Saddles. G. B. Stockton. *The Leather World,* 4, 8-9, 20-21. The hard, tough grain of pigskin makes it superior for saddle leather. Only the best skins can be used, inferior ones being used for belts, purses, etc. Pigskin contains more natural fat than calf and similar skins, and therefore requires special care in the beam house. Since few tanners handle these skins alone, they are apt to be run through with hides, kips or calf. They should be limed in a vat by themselves. After soaking, they are put into an old lime for 24 hours, then taken out, the bath plunged and skins replaced. Next day

Digitized by Google

they are again drawn and worked over the beam on the flesh side with the unhairing knife to remove excess of grease. The lime liquor is strengthened and the skins replaced. This process is continued 12 to 14 days, strengthening every other day. In removing the bristles special care must be taken not to mar the grain, which is quite uneven. Either pigeon- or dog-dung may be used for bating. Two liquors are used; an old one first, for 24 hours. The skins are then scudded on both sides and put into a new bate, made with about 1 pound manure to a skin, remaining 24 hours, or longer if necessary. After a second scudding they are hung in clean water over night. A gambier liquor, increasing from 1° to 8° Bk., is used the first month of tannage, the skins handled every day. The skins are then shaved and hung in the liquor another week. They are then transferred to another pit where they are laid flat with oak bark dusted between and covered with gambier liquor, the liquor being kept at about 12° Bk. and the skins handled once in three days. After 4 or 5 weeks in this pit they are transferred to another, where in addition to the oak and gambier, 5 gallons of quebracho extract is added, making a liquor of 16° Bk. With weekly handling the skins remain here 3 to 4 months, then washed and dried. For saddle work, now select those having perfect grain, and pile damp for one or two days before shaving. The shaving should not be carried quite to the required thickness, leaving a little to be taken off in finishing. After soaking in warm water the grain is brushed and given a hard sleaking, then rubbed over with fine pumice and sleaked again with a dull brass sleaker having rounded corners. A hot dip of quebracho liquor comes next, lasting 3 or 4 days with daily handling. Then rinse and oil lightly on both sides with linseed oil, applied with a piece of flannel. The flesh side is now stuffed lightly with water dubbin, a mixture of cod oil, tallow and cold water. Dry in a moderate heat. The superfluous grease is removed from the flesh with a sharp sleaker, and the grain side moistened with water. The skins are then "whitened" lightly with a small keen-edged knife, and after dampening set out to remove the marks caused by whitening, and then dried again. If a natural color is desired, a finish of Irish moss and gelatine (½ pound moss and 1 ounce gelatine to 5 gallons water) is applied to the grain with a fine brush and the grain rubbed after a time with a damp cloth. After sizing the skins are again dried and boarded, and then sleaked on the flesh and "glassed." Anatto is used where a yellow color is desired, a filtered infusion being applied with a brush and followed with a size of linseed oil and gelatine. If the leather is not stiff enough, Irish moss is applied to the flesh side.

L. B.

The Fungi of Excreta. JAMES SCOTT. *The Leather World*, 4, 21-3. Both bacteria and molds grow in the excreta used for bates and puers. Scott studied the growth of fungi by enclosing dung in a test-tube closed with cotton. The growth may be observed from outside with low mag-

Digitized by Google

nification. Scott believes that the molds aid in the processes of decay necessary to prepare dog-dung for use in puering. Illustrations of several species are given. L. B.

Suede Leather from Foreign Hides. W. EITNER. *Gerber*, 1911 [37] 269. The crude material should be dense in fiber, such as the so-called "wild skins" or certain grades of lamb and sheep skins from Africa and Asia, also the African "blackheads." Formerly hides with poor grain were used, but it is now seen that high grade skins are required.

It is not necessary to sharpen the soaks as some think, for the salt readily takes up water. The aim is to prepare for a firm tannage and the soaking is not pushed after the hides are thoroughly impregnated with water. For salted hides, 2-2½ days soaking in fresh water with one change suffice. For African unsalted hides, the soaks may be sharpened with caustic soda which does not attack the hair like sulphide. In liming, sulphide is used, instead of pure lime which would make this leather spongy, and here it is needful to keep the flesh firm. If the hair is to be preserved, the hides are pasted with calcin, sweated and de-wooled on the beam. They are then swelled in a lime prepared from equal parts of quick-lime and sulphide, 4 kg. of each to 100 pelts. Ordinarily the fells from the soaks go into a used lime for 4-5 days, are then unhaired and put in a fresh sharpened lime for 4-5 days more. The swelling with sulphide, which does not withdraw hide substance, is the most important feature of this process. A dung bate is not suitable here, as for glacé leather, but an acid bate as with lactic acid. This may be derived as a residue in the same manufacture. To carry out the scouring of the fells without loosening the hide substance, the swelling from the limes is meanwhile reduced by applying the residual acid liquor from the bran bate. The cleaned fells generally receive a weak bran bate to make them more receptive of the "Gar" which is composed of 3 per cent. alum, ¾ salt, 5 flour, and ¾ barrelled egg, reckoned on weight of pelt. Latterly a 2 per cent. formaldehyde tannage has been substituted; this cannot be used in combination with albumin with which it reacts. W. J. K.

Dyeing and Currying of Suede Leather. W. EITNER. *Gerber*, 1911 [37] 311-14. To produce the fine plush surface now demanded by fashion, careful mechanical treatment is required. The flesh of the leather is first faced on revolving disks coated with emery, the effect being to cut or shear off the fibers rather than a grinding. After a "broschiren" in luke warm water and wringing out or centrifuging, the moist leather is ground to the desired surface on the grain by holding against revolving hone rollers. Both machine operations are minutely detailed. The writer supplements his earlier papers on dyeing in *Gerber* of 1897, 1898. The fells are softened and stroked with pumice stone to open the plush. Vegetable dyes are principally used, being precipitated by metallic salts, generally alum. Of this, 10 parts are dissolved in 50 parts boiling water

Digitized by Google

with addition of 0.9 parts chalk. The decanted solution is added to the dye decoction in amount insufficient to throw down all the color. Aniline dyes are added to strengthen the colors. For full, bright shades, titanium potassium oxalate is added with the alum. Copper and iron vitriols give dull and dark hues. W. J. K.

The Use of Antichlor in Vegetable Tannage. W. EITNER. *Gerber,* 1911, [37] 297-9. A special preparation in the market, designated "Citol Breil," claiming to greatly improve leather if employed just before tannage, was examined by the author and found to be finely granulated sodium thiosulphate. This salt does not forward tannage aside from what might come from its slight alkaline reaction and its promotion of diffusion. Attempts to utilize various salts on these scores have failed. The author has found antichlor to be a good preservative of hide in case of interruption of the factory process. Trials of the "Citol" according to directions failed to show any utility in leather making. W. J. K.

Substitutes for Expensive Fats. W. EITNER. *Gerber,* 1911, [37] 325-7. Fish oil is the most valuable fat for leather, rendering it soft and waterproof. These properties are due to its tanning action, which is still greater in degras, moellon, etc., which are formed from fish oil in chamoisage. Vegetable oils may be made to produce a similar effect to some extent when applied as fat liquor as used in chrome tannage; a permanent fat tannage results here, differing from ordinary greasing. Certain oils like castor oil produce on treatment with sulphuric acid (sulphonating) a degras substitute. The second important fat for leather is tallow. Its function is to thicken the fish oil, fill the leather and give it a soft feel; it also lightens the color while the fluid oils darken it. Mineral oils are useful in retarding the resinifying action of fish oils, in reducing the stickiness of wool-fat, and in filling leathers without harm. An oil of 0.88 to 0.9 sp. gr. or a wax of 30° melting-point may economically properly replace 25 per cent. or more of fish oil or tallow. Wool-fat is used also as a leather greese, but is properly a filler; it is becoming dear. Rosin oil, coal- and wood-tar oils can be used to some extent. W. J. K.

The Governing Elements in the Tannage of Kips. W. EITNER. *Gerber,* 1912, [38], pp. 1-3, 15-17, 29-31. The soaking often requires especial care, the crude stock being decidedly hard. In general, during the operation of soaking, it is not sufficient to restore the dry hide to its original softness, but also to completely impregnate it with water in order to prepare it for the subsequent liming. Softening by mechanical treatment, as formerly practiced and sometimes at present, does not do this last. On the contrary it is possible that a properly soaked hide, especially when chemicals have been used, may not feel soft but even stiff. After a chemical or "sharpened" soak, an old lime should not be employed, for this may cause considerable loss of hide substance and lower the rendement. The

Digitized by Google

duration of liming is from 5 to 10 days. For upper leathers where the best hides are used, the soaks are but slightly sharpened and the liming follows in the usual plan, in three successive limes to which calcin has been added; sulphide should not be used. It is better that the hide should swell in tanning than during liming. The tendency to excessive swelling in liming of kips which have been chemically soaked often leads to the fault of excessive bating in order to bring down the plumping, thereby weakening the pelt. It is not correct to remove lime plumping by the bate, for this hinders observation of the real office of bating, namely, removal of certain hide material. It is better to delime with acids before bating, and the cheap hydrochloric acid is just as well suited as the more expensive organic acids. The acid should be added portionwise to the bath and not too rapidly, else swelling results from excess of acid. To avoid the risk from free acid, preparations of ammonium butyrate have been substituted which form a soluble double salt with the lime. The delimed hides, if intended for sole leather are next watered to dissolve the lime salt. Hides for upper leather receive a dung bate or for the finer leathers one of the new substitutes, oropon, etc. A common error in small upper leather tanneries is the use of old pine liquors for the fore-tannage. Two cases of this sort from clients reporting defective grain as both loose and brittle are quoted. These troubles originate from too vigorous a bating and a subsequent wasting of the hide in the vats or at least a failure in sufficient filling. The brittle grain is due to presence of butyric acid in the old fermented liquors. During the long time (8 days per vat) in these, the hide is hydrolyzed and a glue-like substance produced which on tannage gives a hard grain. This error is avoided in America where the tannage begins with sweet liquors. It is therefore better for upper leather kips to begin with a Japonica liquor of 6° which is strengthened from time to time, completing in 24-36 hours. This prevents the faults in grain, but to secure a full leather of good weight the old tannage in pine liquors will not do, for these are poor in tannin. It is advisable to strengthen the vats with gambier, or triumph quebracho extract; Argentine extract is entirely unsuitable. To maintain the maximum secured by a rational tannage, careful attention should be paid to the greasing during currying. Only fats having tanning action are suited, such as fish oil, moellon, degras, sod oil; mineral oils fail. Other fats of animal or mineral origin will, however, give weight and make waterproof. These two classes of fats are best applied separately. The fish oil, moellon mixture, etc., is applied in the drum until the leather heats from chemical action, which is then left to finish as the leather dries in the open air. Suitable oils for filling are drummed in hot afterwards.

W. J. K.

Salted Hides in South America. A. R. *Ledertechn Rundschau*, 1911, pp. 385-6. This correspondent describes how the hides are prepared for transportation. If salt be sprinkled on or merely rubbed into the green

Digitized by Google

hide, the product will not withstand heat; salt brine must first be used. The stripped hides are let cool, trimmed and then left stand several hours in salt water of 5° B., then piled and the "blood water" left drain off. The salt bath proper then follows, 20° B., 12-16 hours. The hides are next spread out and piled, 6-10 kg. salt being strewed over each, similar to the layering in tan pits. Sometimes vats are used here to avoid too rapid drainage and drying of the hides. Sea salt gives the best results. Pure salt is not used for strewing, but a mixture of ⅓ new salt, ⅔ used, greasy salt to prevent too vigorous action on the hide. W. J. K.

Testing for Fish Oils. MARCUSSON and VON HUBER. *Chem. Rev. Fett u. Harz Ind.* through *Mat. Grasses,* 1911, [4], 2377. By the action of bromine, fish oils give octobromides which differ from the hexabromides yielded by vegetable drying oils in being very difficultly soluble in benzol. In examining soaps, 10 cc. of total fat acids are agitated with 200 cc. of a solution containing 1 vol. bromine, 28 vols. glacial acetic acid, 4 vols. nitrobenzol, and left stand 1 hour; if no ppt. has formed, fish and drying oils are absent. If a ppt. forms, it is let deposit 2 hours longer, then filtered, washed with ether, dried and weighed. It is then heated with 200 cc. benzol to every 2 grams on the water-bath for ½ hour (reflux condenser); if the solution is complete, fish oils are absent. If insolubles are present, they are filtered hot and dried. If on testing the melting-point there is no fusion below 200° but a partial decomposition with blackening at this temperature, fish oils are proved present. If the melting-point is below 200°, a new extraction is made with benzol to elevate it. The hexabromides from drying oils melt at 175-180° without decomposition.

Fish oils also give directly difficultly soluble bromides (of glycerides) with Halphen's bromine solution; a negative result proves their absence. A ppt. may, however, be due to vegetable drying oils and the brominated glycerides cannot be distinguished. It is necessary to saponify and examine as above. W. J. K.

A Practical Tawed Leather. *Gerber-Courier,* Jan. 20, 1912. Chrome leather has displaced alum tannage in many cases where white leather is required, especially where resistance to water is necessary. Tawed leather has the advantage in color, smooth grain, etc., and by impregnation with tallow may be made highly water-resistant. Hides for white leather were formerly unhaired by scraping, but this is hard to do and is liable to injure the grain. Sweating is better, with special care not to let it proceed too far. The tan-bath is at about 90° F., and contains for 100 pounds white hide, 10 pounds alum, 6 pounds salt and from 15 to 18 gallons of water. In this the hides are milled for 2 or 3 hours, and lie 1 or 2 days. After drying, the leather is moistened and worked to make it soft. Tallow heated to 190° F. is now worked into the flesh side until it begins to come through on the grain. When finished, the grain will be yellowish

Digitized by Google

white. If tan color is desired, the hides are dipped in an extract solution before tannage. By scudding out the fat from the grain an aniline dye or iron black may be applied. L. B.

PATENTS.

Staking Machine. English Patent No. 22,042. W. P. THOMPSON, Liverpool.

Boarding Machine. English Patent No. 23,237. W. FARRAR and S. YOUNG, Bramley, near Leeds.

Rubberizing Hides. English Patent No. 22,716. R. WITHEY, Bermondsey, London.

The hides are steeped in a hot solution of pure para rubber in benzine, coal-tar naphtha, benzol and carbon disulphide, and then transferred to a rotary steam-jacketed drum containing the same solution.

Cylinder for Leather-shaving Machines. U. S. Patent No. 1,016,279. C. A. LOUGEE, Newark, N. J.

Waterproofing Compound for Leather. U. S. Patent No. 1,016,137. P. F. FROST, Silverdale, Wash.

The compound is two-thirds melted tallow, one-fourth oil of tar and one-twelfth melted rubber, with a luster-giving substance.

Evaporating Apparatus. U. S. Patent No. 1,016,160. P. KESTNER, Lille, France, assignor to Kestner Evaporator Co., Philadelphia.

Machine for Removing Bark from Logs. U. S. Patent No. 1,015,898. FRED LIBERT, Green Bay, Wis.

Separator for Vacuum Pins. U. S. Patents Nos. 1,015,629 and 1,015,704. GEORGE M. NEWHALL, Philadelphia, Pa.

Apparatus for the Evaporation to Dryness of All Liquids, Tanning Extracts, Etc. French Patent No. 429,564. R. JOYA, Isere, France.

A wheel dips into the liquid, and revolves in a space through which a current of warm air is forced. The dried material is automatically scraped off the slowly revolving wheel.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII APRIL, 1912 No. 4

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members. $5.00 annually; Non-members. $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

ELECTIONS.

ASSOCIATE.

Arthur T. Brainerd, 317 North Clark St., Chicago, Ill.
J. C. Cover, c/o Vacuum Oil Co., 29 Broadway, New York City.
Samuel A. Faust, Amber, Montgomery County, Penna.
Frank S. Havens, 3500 Grey's Ferry Road, Philadelphia, Penna.
Elting C. Stillwell, 66 Clifton Place, Brooklyn, New York.

CHANGES OF ADDRESS.

H. S. Frederick to 810 Court St., Sault Ste. Marie, Mich.

A. A. Whiting, to 621 Oakwood Boulevard, Chicago, Ill.

Adolf Schubert, to 1828 Myrtle Ave, Ridgewood, Queens Co., New York, N. Y.

Digitized by Google

COUNCIL MEETING.

A meeting of the Council was held in New York City, Friday, March 1st, the following members being present:—Messrs, Veitch, Griffith, Reed, Teas, Hoppenstedt, Small and Oberfell.

H. C. Reed, F. H. Small and J. H. Yocum were appointed a committee to re-write the method of tannin analysis and to report by April 1st.

The following subjects were selected for collaborative committee work:

The Disposal of Tannery Waste, F. P. Veitch, Chairman.

Analysis of Fats and Oils, C. R. Oberfell, Chairman.

The Determination of the Acidity of Liquors and the Matter of a Proper Preservative. Ionization, Lloyd Balderston, Chairman.

Leather Analysis, F. P. Veitch, Chairman.

Proper Sampling of Leather for Analysis, F. H. Small, Chairman.

Salt Stains on Hides, J. H. Yocum, Chairman.

The Detection and Estimation of Tanning Materials in Admixture, A. W. Hoppenstedt, Chairman.

The Analysis of Sulphite Cellulose Extracts, F. H. Small, Chairman.

Color Tests for Tanning Materials, A. W. Hoppenstedt.

The Analysis of Lactic Acid, the Secretary authorized to select a chairman of the committee.

The Editor was instructed to publish the following recommendations which occurred in the report of the Leather Analysis Committee for 1911. The Council has decided that these are merely explanatory of the determination of fats and oils in leather and as such has decided to incorporate them in the method, unless there is serious objection.

Recommendations:

1. For fats, in the sentence after leather insert "Placed loosely."

2. At the end of the first sentence insert "syphoning should occur from 8-10 times per hour and continue 6-10 hours with leathers containing much grease."

Digitized by Google

This paragraph of the Official Method for Leather Analysis will therefore read as follows:

(3) Fats:

Extract 5 to 10 grams of air-dry leather placed loosely in a Soxhlet apparatus until free from grease, using petroleum ether boiling below 80° C. Syphoning should occur from 8-10 times per hour and continue 6-10 hours with leathers containing much grease. Evaporate off the ether and dry to approximately constant weight.

Or, if preferred, extract 30 grams of leather as described above. In the latter case, the extracted leather, when freed of solvent, may be used for the determination of water-soluble material.

TANNIN PLANTS OF PARAGUAY.

Exhibited at the International Agricultural Exposition, held at Buenos Aires, 1910.

By. Dr. W. W. Stockberger.

The tannin plants discussed in this paper comprise those listed in the catalogue of the Paraguay exhibit[1] at the International Agricultural Exposition, Buenos Aires, 1910. Some of the species mentioned occur in other countries and certain ones have been more or less thoroughly examined with respect to their possible utilization as a commercial source of tannin. Supplementary notes on these and some related species have been added. The plants are arranged according to the family to which each belongs, and the italicised specific name of each is followed by the native name in parenthesis. Percentages of tannin refer to the bark except where otherwise stated.

Following is the list of plants:

FAMILY PALMAE.

Cocos romanzoffiana Cham. (Pindo) contains 6.6 per cent. tannin, used by the natives to tan fine hides. A palm-tree abundant in all the forests along the coast where it is inconsiderately destroyed in order to obtain the leaves which make fine green forage for the droves of mules used by the lumber firms.

[1] Catalogo descriptivo de los productos expuestos por la Estacion agronómica de Puerto Bertoni, Paraguay, Asuncion, 1910.

Digitized by Google

FAMILY ANONACEAE.

Rollinia sp. (Aratikú gwazú) contains 4.2 per cent. tannin. A tree, often quite tall, common in the forests and well known for its fruit. The thin bark abounding in bast fibers is easily removed. Color when freshly broken, grayish.

The bark of *R. salicifolia* Schlecht., which occurs also in Brazil, is used as an astringent. According to Peckholt[2] the leaves and roots of the Brazilian species *R. sicberi* D. C., and the unripe fruit and bark of *R. exalbida* Mart., are used as astringents.

FAMILY LAURACEAE.

Ocotca sp. (Yhvá-ikâ) contains 10.8 per cent. tannin accompanied by a mucilaginous substance in large proportions. The bark contains few fibers, and the color when freshly broken is grayish. A stout tree, often quite tall, common in the forests of Paraguay, utilized at times for its timber.

A species of this genus, *O. bullata* E. Mey., which occurs in Cape Colony, South Africa, contains according to Juritz[3] 5.8 per cent. tannin.

FAMILY CAESALPINIACEAE.

Apuleia praecox Mart. (Yhvihrá-perè) contains 10.7 per cent. tannin. Bark smooth, somewhat difficult to remove, color when freshly broken pale yellow. A stout tree, fairly common, used for lumber.

Copaifera lansdorfii Desf. (Kupaih) contains 16.6 per cent. tannin and a certain proportion of resinous matter. Bark thick, ligneous, the corky layer readily breaking into small fragments, fracture whitish red. A tree with well developed trunk, abundant in the forests along the course of the river Mondá-íh, rare in other places. It is from this tree that the Jesuit Missionaries extracted a fragrant balsam known in commerce under the name balsam copaiba.

In Guiana the bark of *C. bractcata* Benth. is said to be used for tanning.[4]

[2] Peckholt, Th. "Heil- und Nutzpflanzen Braziliens aus der Familie der Anonaceae," *Berichte d. deut. Pharm. Ges.*, 1897, p. 450.

[3] Juritz, C. F., "Noodzakelijkheid voor georganiseerd scheikundig onderzoek in de Kaapkolonie: looistofbepalingen," *Landbouwjournaal Kaap de Goede Hoop*, 1905, p. 538.

[4] Niederlein, G., "Ressources végétales des Colonies françaises," Paris, 1902.

Digitized by Google

FAMILY MIMOSACEAE.

Enterolobium timboüva Mart. (Timbó) contains 22.3 per cent. tannin and a certain quantity of resinous matter. Bark thick with corrugated epidermis and woody bast, fracture of the young bark white, mature bark reddish. A tree frequently attaining a very large size, quite common, and utilized for lumber. Regarded by the natives as a superior tanning material which gives a special quality to the leather.

The bark and pods of *E. cyclocarpum* (Jacq.) Griseb., occurring in Mexico and Central America, are said to be rich in tannin.

Inga affinis D. C. (Ingá gwazú) contains 25.8 per cent. tannin. Bark smooth, brittle, very deficient in bast fibers, easily separated from the trunk, fracture whitish red. A tree, sometimes quite stout, growing in profusion on the banks of rivers and small streams.

Mimosa sp. (Yukerí guazú) contains 10.8 per cent. tannin. Bark thick, epidermis somewhat corrugated and quite ligneous, fracture dark red. A tree with spiny branches, common in certain places.

The roots of the Indian species *M. pudica* L. contain 10 per cent. tannin[5] and the bark of *M. farinosa* Gris. from Argentina yields 3.9 per cent.[6] In China the bark of *M. sensitiva* L., which occurs in Central America and the East Indies, is used as an astringent.[7]

Peltophorum dubium Taub. (Yhvihrá puihtâ) contains 31.2 per cent. tannin and a large quantity of coloring matter. Bark thick and corrugated, exceedingly ligneous, easily detached from the trunk in long strips, fracture red. A tree, widely used for timber, at times reaching an extraordinary size, common throughout the entire region.

Piptadenia rigida Benth. (Kurupaih-râ puihtâ) contains 28.2 per cent. tannin and coloring matters in moderate proportions. Bark ligneous, epidermis checked and corrugated, easily detached from trunk, fracture pale rose. A tall tree at times rivalling the

[5] Hooper, D., "Indian tanning materials," *Amer. Jour. Pharm.*, Vol. 24, 1894, p. 377.

[6] Levi, L. E. and J. F. Sigel, "Analysis of Cuban and Argentine barks, woods, leaves and fruits," *Hide and Leather*, 1905.

[7] Dekker, J., Bull. Kolo. Museum, Haarlem No. 35, 1906, p. 127.

Digitized by Google

large cedars in size. Another common species known as Kurupaih-râ morôti is equally rich in tannin.

The bark of *P. cebil* Gr., from the Argentine, is reported to contain 15 per cent. tannin.[8]

FAMILY FABACEAE.

Dalbergia sp. (Yhsapih-íh) contains 5.8 per cent. tannin. Bark smooth, easily removed, slightly ligneous, fracture blackish. A stout tree which is very abundant.

A decoction of the bark of the Indian species *D. latifolia* Roxb., according to Dekker,[9] is very astringent.

FAMILY MELIACEAE.

Cabralea sp. (Cancharana) contains 5 per cent. tannin in the young bark. Mature bark rather thick, somewhat fibrous, a little hard to remove and of whitish fracture. A well-developed tree, used at times for lumber, profusely abundant in the forests.

"Cedrela tubiflora" (?) (Cedro) contains 12.6 per cent. tannin. Bark quite thick, composed of tenuous and fibrous layers superposed; corky portion fissured; easily removed, fracture irregular, reddish. A tree common in the entire region, widely used for timber. Two other species also occur which contain about the same per cent. of tannin.

Guarea sp. (Guaré) contains 10.02 per cent. tannin. Bark ligneous, easily removed, fracture whitish. A tree of medium development, abundant.

Among other species of this genus containing tannin are *G. grandiflora* D. C., Java, and *G. trichilioides* L., Guiana, the bark of which is used in tanning.[10]

Trichilia hicronymi Griseb. (Kaátiguá morôti) contains 23 per cent. tannin and a large proportion of coloring matter in the bark, which is smooth, readily removed in longitudinal strips, easily broken. The fracture is whitish red. A small tree common everywhere, the bark of which is frequently used by the natives to tan hides and to dye cotton fabrics a yellow rose color.

[8] Levi, L. E. and J. F. Siegel, "Analysis of Cuban and Argentine barks, woods, leaves and fruits," *Hide and Leather*, 1905.

[9] Dekker, J., "De looistoffen," Bulletin Koloniaal Museum, Haarlem, No. 35, 1906, p. 132.

[10] Höhnel, F. R. von, "Die Gerberinden," Berlin, 1880.

Digitized by Google

Trichilia catigua A. Juss. (Kaátiguá puihtâ) contains 20.5 per cent. tannin and a heavy proportion of coloring matter. Fracture of the bark, dark orange. In other respects like the preceding but somewhat less appreciated as a tanning agent, since it gives a harshness to the leather.

FAMILY EUPHORBIACEAE.

Alchornea triplinervia Muell. (Tapiá gwazú-ih) contains 11.7 per cent. tannin. Bark quite thick, without bast fibers, texture granulose and fragile, easily removed, fracture reddish. A well developed and abundant tree.

"Croton succirubrum" (?) (Sangre de Drago) contains 11.7 per cent. tannin and a resinous matter of a penetrating odor. Bark smooth, thin, quite fibrous, easily removed from sap-wood, fracture white. A small tree, abundant along the rivers but rare in the forests of the uplands.

FAMILY SAPINDACEAE.

Allophylus edulis Radlk. (Kôkû) contains 10 per cent. tannin. Bark smooth, thin, without bast fibers, somewhat adherent to the sap-wood whence very difficult to remove, fracture yellowish white. A small tree common in certain places but of scant development.

Cupania uraguensis Hook & Arn. (Kambuatâ) contains 17.5 per cent. tannin. Bark rather thick, ligneous, very adherent to the sap-wood, removable only in small pieces by hammering, fracture reddish. A tree of moderate dimensions, characteristic of the forests bordering the rivers and small streams.

Cupania vernalis Cambess. (Yaguarataíh) contains 15 per cent. tannin. Bark smooth, somewhat ligneous, easily removed in large strips, fracture pale rose. Small tree more common than the preceding species.

Cupania sp. (Cedrillo) contains 15.8 per cent. tannin. Bark thin, fibrous, somewhat adherent to the sap-wood, fracture whitish rose. A small tree of scanty development, usually growing in low places on banks of rivers and small streams. Preferred by the natives for tanning fine skins.

Digitized by Google

FAMILY GUTTIFERAE.

Rheedia brasiliensis Planch & Trianan. (Pakurí) contains 21.6 per cent. tannin and a small proportion of resinous and coloring matters. Bark smooth, easily removed, brittle, fracture pale red. A fruit-bearing tree, well known, and common in the forests, height ranging from 12 to 14 meters, but small in diameter.

FAMILY MYRTACEAE.

"Britoa fragrantissima" (?) (Yhváviró) contains 9.2 per cent. tannin. Bark smooth, thin, somewhat fibrous, easily removed, fracture whitish. A small fruit-bearing tree of small development. Grows in abundance at times in the old "capueras."

"Campomanesia guavirá" (?) (Yhvávirá) contains 11.6 per cent. tannin. Bark thin, fibrous, difficult to separate from the trunk, fracture whitish yellow. A fruit-bearing tree known and esteemed in all parts of the country, frequently reaching large size, common everywhere.

Eugenia brasiliensis Lam. (Yhvá-poroítih) contains 43.4 per cent. tannin in the mature bark, 16.6 per cent. in the dry leaves and 11.6 per cent. in the wood with little resinous and coloring matter. Bark whitish externally, smooth; without bast fibers, very adherent to the sap-wood, especially when the flow of sap is scanty, fracture color of hazel-nut. Well known fruit-bearing tree from 5 to 10 meters high, 30 to 45 cm. in diameter. Abundant in the forests where in certain low places it forms dense thickets.

Eugenia michellii Lam. (Nangapirih gwazú) contains 28.5 per cent. tannin and very little other extractive matter. Small tree 5 to 7 meters high, small diameter. Bark smooth and thin, somewhat ligneous, fracture whitish. Abundant in low grounds, on banks of small streams and rivers, together with other species of the same genus, similar and all more or less tanniferous.

Eugenia pungens Berg. (Yhvá viyú) contains 10.8 per cent. tannin. Bark thin, smooth, exceedingly adherent to the sap-wood and very difficult to remove, texture fragile, fracture cinnamon color. A fruit-bearing tree, as well known and valued as *E. brasiliensis,* but larger in size and less common.

Eugenia sp. (Regalito) contains 15.8 per cent. of very pure

Digitized by Google

tannin. Bark smooth, not very thick, adherent to the sap-wood, removable only in small pieces, fracture color of hazel-nut. A small tree 5 to 7 m. high, 15 to 25 cm. in diameter. Less abundant than the other species of the same genus.

Eugenia sp. (Yhvájhay puihtâ gwazú) contains 28.7 per cent. tannin. Bark smooth, thin, without bast fibers, easily removable, fracture whitish. A tree 10 to 12 meters high, 30 to 50 cm. in diameter, not very abundant.

This genus is widely distributed and many of its species contain a relatively high per cent. of tannin. Hooper[11] found 19 per cent. in the bark of *E. jambolana* Lam., from India, 12.4 per cent. in *E. jambos* L., from Brazil, 16.1 per cent. in *E. arnottiana* Wight, 11.9 per cent. in *E. montana* Wight, and 10.1 per cent. in *E. caryophyllifolia* Wight; Maiden[12] reported a content of 16.9 per cent. in the bark of *E. smithii* Poir, from Australia, and Höhnel[13] 16 to 17 per cent. in *E. maire* A. Cunn., from New Zealand. The bark of *E. operculata* Roxb., from Sumatra, according to Bernardin,[14] and that of *E. ovigera* Brongn. and Gr., from New Caledonia, according to Niederlein,[15] is used for tanning.

"Myrtus edulis" (?) (Yhvá mbopi) contains 21.8 per cent. tannin. Bark thin, smooth. Somewhat difficult to remove, fracture whitish.

FAMILY SAPOTACEAE.

Bumelia obtusifolia R. and S. (Pihkasúrembiú) contains 8.4 per cent. tannin. Bark smooth, somewhat ligneous, easily removed, fracture whitish yellow. A tree of moderate size, somewhat abundant.

FAMILY APOCYNACEAE.

Aspidiosperma polyneuron Muell. (Palo Rosa) contains only 2.6 per cent. tannin. The wood contains a pink coloring matter

[11] Hooper, D., "Indian Tanning Materials," *The Agricultural Ledger*, Calcutta, 1902, No. 1.

[12] Maiden, J. H., "The Useful Native Plants of Australia," London, 1889, p. 327.

[13] Höhnel, F. R. von, "Die Gerberrinden," Berlin, 1880.

[14] Bernardin, M., "Classification de 250 matières tannantes," Ghent, 1872.

[15] Niederlein, G., "Ressources végétales des Colonies francaises," Paris, 1902.

Digitized by Google

of possible usefulness. A tall, stout tree, yielding excellent timber, at present neither well known or much used. Found only in some places in Paraná north of the parallel of 26°.

The White Quebracho, *A. quebracho-blanco* Schlecht., from the Argentine, contains in the wood about 3 per cent. tannin, in the leaves 27 per cent. and in the bark 4 per cent.[16]

FAMILY BIGNONIACEAE.

"Tecoma ipé araliácea" (?) (Lapacho) contains 5 per cent. tannin. Bark thick, bast fibers abundant, epidermis and corky portion cracked or fissured, easily removed, fracture whitish. A well known and common tree, one of those most used for timber.

According to Niederlein[17] the bark of *T. leucoxylon* Mart., from Guiana, is used in tanning.

U. S. DEPT. OF AGRICULTURE,
BUREAU OF PLANT INDUSTRY.

THE VALUE OF THE NON-TANS IN TANNING MATERIALS AND EXTRACTS.[1]

By Dr. J. Gordon Parker and J. R. Blockley, M. Sc.

The experiments recorded in this paper were undertaken as an attempt to determine what influence the non-tanning matters in an extract or material have on the penetration of the tanning matters, on the increase in weight of leather and what leather forming properties the "non-tans" possess. This subject has been investigated by one of us by experiments on a practical scale (*Journal of the Society of Chemical Industry*, March 31, 1910),[2] but it had not been determined by chemical methods what part the non-tans actually played. In the paper referred to, it is stated that "This question has become more acute of late years, owing to the introduction of closed autoclaves for the extraction of the wood in the manufacture of extracts, instead of open extraction

[16] Möller, Jos., "Ueber das Quebrachoholz," *Dingler's Polytech. Journ.*, Vol. 230, 1878, p. 481, 845.

[17] Niederlein, G., "Ressources végétales des Colonies francaises," Paris, 1902.

[1] *J. S. C. I.*, Vol. 30, No. 24, p. 1433-7.

[2] This JOURNAL, Vol. 5, p. 297.

Digitized by Google

vats. This has resulted in the manufacture of what are commonly called 'pressure extracts,' *i. e.*, extracts which are manufactured by extracting the material from which they are made under pressure of one or two atmospheres." The result of this pressure extraction is that there is a greater yield of soluble substances, but also a decomposition of a certain amount of tannic acid. This shows itself in the analysis, for in the extract obtained by pressure extraction, the amount of non-tans is very much higher than in the extract obtained by open extraction. It is sometimes claimed that this higher percentage of non-tans penetrates the fibers of the leather and thus gives a higher yield. This is particularly the case, it is stated, with drum tannage. The object of this investigation was, therefore, to find out how far the non-tans in an extract do actually penetrate the fibers and give weight to the leather. From the experiments already published it was concluded that as regards actual tanning of leather, better results were obtained both for weight and firmness with an extract containing a low percentage of non-tans, or at least, it was claimed that the higher percentage of non-tans had not in any way contributed either to weight or firmness.

In the following experiments, pieces of pelt were tanned out in liquors made from various extracts. These liquors were made to contain varying percentages of non-tans by the addition of "non-tanning" matters separated from the original extract. Liquors were thus obtained containing the same percentage of tannin, but varying percentages of non-tans. By tanning out pieces of pelt in these liquors the influence of the amount of non-tans on the rate of penetration of the tan and on the yield of leather could be ascertained.

A. *Experiments with Chestnut Extract.*

The first series of experiments was carried out on a well-known chestnut extract. This extract gave the following figures on analysis by the official I. A. L. T. C. method:

	Per cent.
Tanning matters	28.6
Non-tanning matters	12.5
Insoluble	0.9
Water	58.0
	100.0

Digitized by Google

A solution containing nothing but non-tanning matter was made from this extract as follows:

Three hundred and twenty grams of the extract were dissolved in 2 liters of distilled water and 2 liters of 5 per cent. gelatine solution were added. This caused the precipitation of most of the tanning matters. The completion of the detannization was effected by churning with chromed hide powder as in the ordinary I. A. L. T. C. method of tannin analysis. Total detannization cannot be effected with gelatine alone as the end point is not at all defined, but by adding too little gelatine to precipitate the whole of the tannin and then completing the detannization with hide powder, results were obtained which agree fairly closely with the results to be expected from the official analysis of the extract. That is, the amount of "non-tans" in the resulting solution was nearly the amount calculated from the original analysis. In this way a solution containing 1 per cent. of non-tanning matters was obtained.

By means of distilled water and of this solution of non-tans, solutions of the extract were made as follows:

A. Two hundred and ten grams extract dissolved in 2 liters of water giving a solution of 3 per cent. of tans, and 1.31 per cent. non-tans and of Barkometer strength of 15°.

B. Two hundred and ten grams extract dissolved in 1 liter of water and 1 liter of the non-tan solution, giving a solution of 3 per cent. of tan, 1.81 per cent. non-tans and of Barkometer strength of 17°.

C. Two hundred and ten grams extract dissolved in 2 liters of the non-tans solution, giving a solution of 3 per cent. of tan, 2.31 per cent. of non-tans and Barkometer 19°.

Calculated back on the original extract the figures give:

	Per cent. of tan	Per cent. of non-tans.
A	28.6	12.5
B	28.6	17.3
C	28.6	22.0

Pieces of pelt from a butt in as uniform a condition as possible were cut up into strips of 2 inches by 4 inches and delimed with boracic acid. Three of these pieces were taken for each test. Tannage was commenced in liquors of ½ per cent. of tan and was continued until no further absorption took place, finally fin-

Digitized by Google

ishing the tannage in liquors containing 3 per cent. of tan. The liquors were strengthened up gradually and uniformly for the three tests. The pieces were tanned in jars which were put in a rotating churn for several hours per day, the tannage taking three weeks. At the end of this time the pieces were taken out, scoured, oiled, partially dried, rolled and dried out. Samples were taken during the tannage and analyzed and the finished leathers were analyzed. The following table shows the amount of absorbed matter per 100 parts of original hide:

A	After 3 days	After 10 days	After 21 days
A	59.7	87.3	98.0
B	52.5	85.0	96.0
C	51.3	85.0	96.4

It will be seen from these figures that the amount absorbed with an excess of non-tans is less than with no added non-tans, a result in accordance with Stiasny's work (*Collegium*, 1909, p. 395). At first the penetration is considerably retarded but the total amount absorbed after complete tannage is almost the same. To see if the tan which had been absorbed had actually combined with the hide fiber the resulting leathers were analyzed with the following results:

	Moisture	Matter washed out by water	Mineral matter	Hide substance	Combined tannin	Degree of tannage
A. No added non-tans	14.0	12.6	0.8	42.6	30.0	70.4
B. 5 per cent. non-tans added	14.0	13.0	0.8	43.1	39.1	67.5
C. 10 per cent. non-tans added	14.0	13.3	0.8	43.0	28.9	67.2

Although the total amounts of leather formed from the three solutions do not vary very much, it will be seen that the quality of the leather produced is not the same in each case. The figures in the second column give the amount of soluble matter in the leather, *i. e.*, the amount of matter which can be washed out by water. The leather tanned with the excess of the non-tans contains more of this than the others do.

The figures in the last column give the amounts of tanning matter actually combined with 100 parts of hide fiber, and the "degree of tannage" is the best criterion of the amount of actual tannage which has taken place. It will be observed that the most

Digitized by Google

thorough tannage has taken place when there was no excess of non-tans, and it appears that the non-tans have a retarding influence on the penetration of the tannins.

A further series of experiments were made on the same extract and in the same way as the above, with the exception that the pieces of leather were not tanned in rotating jars but merely by suspension. This was to make the two series run as parallel as possible to the drum method, and to the ordinary suspension method of tannage, respectively. The strengths of liquors were the same as for the previous tests and the time of tannage was the same. The results of the analysis of the resulting leather were as follows:

	Moisture	Mineral matter	Matter washed out by water	Hide substance	Combined tannin	Degree of tannage
A. With no added non-tans	14.0	1.0	12.1	44.8	28.1	62.7
B. With 5 per cent. added non-tans.	14.0	1.0	12.3	45.6	27.1	59.4
C. With 10 per cent. added non-tans.	14.0	1.0	12.3	46.5	26.2	56.4

In this "still" tannage the amount of water soluble matter is about the same for each case, but the degree of tannage shows even wider divergencies than is the case of the "drum tannage," a difference of 6 existing between the degrees of tannage of the leather tanned with no added non-tans, and of the leather tanned with 10 per cent. of added non-tans.

B. *Tests with Oakwood Extract.*

The oakwood extract used was one well known on the market. The I. A. L. T. C. method of analysis gave:

	Per cent.
Tannin	29.0
Non-tannin	14.7
Insoluble	0.2
Water	56.1
	100.0

A solution containing only non-tans was made as before by detannizing first with gelatine and finally with chromed hide powder. In this way a 1 per cent. solution of non-tans was prepared. With distilled water and with this solution of non-tans,

Digitized by Google

liquors containing the same percentage of tan but different percentages of non-tans were obtained:

	Per cent. of tan.	Per cent. of non-tan.	Barkometer
A	3.0	1.5	18°
B	3.0	2.0	20°
C	3.0	2.9	24°

Calculated back on the original extract the figures give:

	Per cent. of tan.	Per cent. of non-tans.
A	29.0	14.7
B	29.0	19.5
C	29.0	28.0

Pieces of pelt were taken as before, cut into strips, delimed and tanned in liquors made from the above solutions. Tannage was commenced in liquors containing 0.5 per cent. of tan and finished in liquors containing 3 per cent. of tan, the liquors being uniformly strengthened for the three tests. The resulting leathers were finished and dried out as before and on analysis gave the following figures:

	Moisture	Mineral matters	Water soluble matter	Hide substance	Combined tannin	Degree of tannage
A. No added non-tans	14.0	0.4	15.2	47.2	23.2	49.2
B. 5 per cent. non. tans added	14.0	0.4	15.3	47.5	22.8	48.0
C. 13 per cent. added non-tans	14.0	0.4	15.3	49.0	21.3	43.5

The amount of water soluble matter is the same in each case, but the amount of tan actually combined with hide fiber shows very great variations. Here again the presence of the additional non-tans exerts a retarding influence on the penetration of the tan.

Still Tannage.

A similar series of experiments was conducted, tanning out the pieces of leather by suspension only without giving any "drumming." The results were very similar to the above and the non-tans played the same part in reducing the amount of tan combined with the fibers.

C. A third series was carried out to bring the conditions as close as possible to the conditions which actually obtain in practice.

Digitized by Google

It might be argued that the above experiments do not give a fair indication of what is likely to take place in practice. The chief objection which could be urged would be that the tannage was conducted in liquors which contained no natural acids. To meet this objection the following plan was adopted:—A solution of non-tanning matters was made from the same chestnut extract as in the first series (A), and solutions of the same percentage of tan but different percentages of non-tans were prepared as before, but to each of these solutions was added the same quantity of a tan liquor taken from a top suspender liquor and containing a fair amount of acidity. The addition of such a liquor made the resulting liquors more closely approach the liquors actually used in practice.

Solutions were thus made as follows:

	Per cent. of tan.	Per cent. of non-tans.
A	3.0	1.31
B	3.0	1.81
C	3.0	2.31

and to 2 liters of each of these solutions was added 500 cc. of suspender liquor of acidity 10 cc. = 15 cc. N/20 lime water.

Pieces of pelt were taken as before and tanned out in the above solutions. After tanning they were taken out and finished as before and analyzed. Two series were performed, one in rotating jars and the other by suspension. The leathers tanned in the first series, *i. e.*, by the drum tannage, gave the following results on analysis:

	Moisture	Mineral ash	Water soluble matter	Hide substance	Combined tannin	Degree of tannage
A. No added non-tans	14.0	0.7	11.1	48.1	26.1	54.3
B. 5 per cent. added non-tans	14.0	0.8	10.9	47.7	26.6	55.8
C. 10 per cent. added non-tans	14.0	0.6	10.7	49.5	25.2	50.9

The same general effect is apparent as in the first series although not to such a large extent. The difference in the degrees of tannage between the leather tanned with no added non-tans and with 10 per cent. added non-tans, is 3½ in favor of the former.

A similar series to the above was performed but the pieces were tanned by suspension instead of by the drum:

Digitized by Google

	Moisture	Mineral ash	Water soluble matter	Hide substance	Combined tannin	Degree of tannage
A. No added non-tans	14.0	0.6	9.2	48.4	27.8	57.4
B. 5 per cent. added non-tans	14.0	0.4	8.8	51.4	25.4	49.4
C. 10 per cent. added non-tans	14.0	0.4	9.8	50.8	25.0	49.0

The effect of the non-tans on the penetration of the tannin was more marked than with the drum tannage, there being a difference of 8 between the degrees of tannage produced by solutions A and C.

It appears from all the above experiments that the non-tanning matters have a retarding influence on the penetration of the tan and that the total yield of leather is reduced.

One influence of the non-tanning matters is in the production of acidity. Some of the liquors used in the above tests were allowed to stand, and the amount of acid developed was measured from time to time. In every case the amount of acid was greatest in the liquors with the most non-tans. The following table shows the results of two of the series:

1. CHESTNUT.

	C.c.s. of N/20 lime water per 10 c.c.s. liquor	
	After 1 month	After 2 months
A	6.4	6.6
B	7.0	7.3
C	7.5	8.1

2. OAKWOOD.

	C.c.s. of N/20 lime water per 10 c.c.s. liquor	
	After 1 month	After 2 months
A	5.0	5.8
B	5.8	6.9
C	8.5	9.5

The effect is the one naturally to be expected, that the non-tans produce acids by fermentation.

DISCUSSION.

The CHAIRMAN said that the paper claimed to have established two points. First, that the absorption of tannin was delayed by the presence of non-tanning materials, and secondly, that the non-tans were not absorbed. It seemed to him that the first contention was clearly proved, for on the results obtained there was

Digitized by Google

evidence of a retardation of the absorption of the tannin. But on the second point he desired to ask whether there was not sufficient variation in the non-tannin substances to make it a matter for consideration how the non-tans with which they experimented should be prepared. The authors had prepared their non-tans by removing the tannins by means of hide. Was there not a danger that by selective absorption the more readily available non-tans had also been removed? If so, the rate of absorption of the residual non-tans would not be that of what might be termed a whole extract.

MR. C. F. CROSS said that the authors would agree there must be a linking series of carbohydrate bodies derived from the parent wood (or bark) substances which undoubtedly played a very direct and specific part in tanning processes. It was also clear that by removing them, as had been done in this case, the tanning liquors were fractionated in a very artificial way, consequently the incidence of the argument was limited to a technical point as between himself and extractors. He thought Dr. Parker would admit there was a larger question remaining to be solved by tanners: that was, what was the function in the tanning process of this series of colloidal carbohydrate "non-tans" which existed in association with the aromatic tanning bodies and in the plant, and what useful modifications of the process might be expected from additions of such non-tans?

MR. W. P. DREAPER asked Dr. Parker exactly what he thought was the part played by gallic acid. Under modern conditions of analysis in tanning, the whole trend seemed to be to prevent the absorption of gallic acid by the material which was used to determine the percentage (say 30 per cent.) of "tannin" present. Some few years ago Mr. Wilson and he (*J. S. C. I.*, 1906, **25**, 515) had read a paper dealing with the absorption of gallic acid by tannic acid coagulum, and they proved, in addition to the fact that gallic acid was absorbed, it materially altered the physical nature of the coagulum. If the authors were working in the presence of gallic acid and calling the non-tans something which was minus gallic acid, were they correct in making the tests recorded and assuming, as the Chairman said, that the non-

Digitized by Google

tans dealt with in this paper really represented the ordinary non-tans as gauged by analysis or actual working?

Dr. S. Rideal said it seemed to him that the question was whether it was necessary to form a definite compound of the tannin with the hide substance in the finished article, or whether the leather user was content to buy a product which had weight and other desirable properties. If the 70.4, the 67.5, and the 67.2 were the ultimate percentages they could get by the introduction of tannin into the hide substance, and those figures practically represented the finished product, it was obvious that the first one, the 70.4, was a better tannage than the one with 67.2; but as they had all three been done at the same time, and the weight in the second and third was less, some of the other substances had gone in to make up the 100 per cent. of the total weight, and one would like to know, before passing a final opinion, what the general physical properties of these finished products were, and not simply base an opinion on the percentage of tannin in the three. He would have liked to have known something of their tensile strengths and their waterproof capacities, their loss of weight on wearing, and attrition tests before giving a definite answer to that particular question.

Mr. J. R. Blockley, in reply, said their method of preparing the non-tans was to take a solution containing the extract as it was and detan it, first with gelatine and then with hide powder, so that the final product was similar to that obtained in tannin analyses, and the whole question was to see if the non-tans, as given by analysis, really did affect the penetration of the tans. The differences between some of the tanning and non-tanning matters were not so well known that any very definite distinction could be drawn between them except by the method of the hide powder analysis, and he thought in that case it had been clearly shown, as given by this means of differentiating them from the tannins, that the non-tans did retard the penetration of the tans. It was unfair to compare these non-tanning matters with others, say, the new colloids, which made leather but which were supposed to be non-tans according to analysis, because in this case the medium was a water solution, and in the case of the new materials the tannage is conducted without the medium of

Digitized by Google

water. With regard to some of the physical properties of leather, in addition to the degrees of tannage which were usually accepted by a chemist as giving a fair indication of the quality of the leather, they also measured the amount of soluble matter in the leather, that was, the amount of matter which could be washed out by the ordinary method of washing with water, and in most cases they found relatively more soluble matter was washed out in those cases where they had the most non-tans. That was generally taken to mean that the leather was less waterproof. The samples they had dealt with were too small to attempt any method of determining the wearing properties; but they took the soluble matter and degree of tannage as a fair indication of the quality of the leather. One point which had been urged before was, that in a drum tannage, probably the increase in the quantity of the non-tans would have a greater effect than in a "still" tannage; that was by simply suspending the hides in liquors, and in the drum tannage, the tannage by mechanical motion. It had been said that perhaps in the drum tannage more of the non-tans would penetrate than in the still tannage. As a matter of fact, their degrees of tannage showed the same variations as in the still tannage, but in the drum tannage they got a higher amount of soluble matter in the leather than by the still tannage, and the amount of water-soluble matter was higher in the case where they got the most non-tans.

Dr. Gordon Parker, in reply, said the amount of soluble matter washed out in A was 12.6 per cent.; in B, 13 per cent., and in C, 13.3 per cent. The difference was very small, but when worked out on percentage it made a greater difference. In one case there were 170 parts of leather substance, in another 167½, and in the third 167¼. Of the 170, 12½ were washed out, and dealing with a much lesser amount of leather, 13; so that really the result was magnified in that way, and that should be taken into consideration. In answer to the Chairman's point as to whether the non-tans were absorbed, he did not think the matter was definitely settled yet. Certain non-tannins undoubtedly were absorbed. Non-tannins were distinctly advantageous to the tan. Their chief advantage undoubtedly was the formation of acids which plumped and swelled the fibrous tissue so that it might

Digitized by Google

easily absorb the tannic acid, but whether the glucosides and some of the substances which were naturally present in wood extracts (made by extraction under pressure) were absorbed was questionable, because they had tried on many occasions in their experimental tannery, where they tanned some 20 hides a week, to find out, by taking the liquors high up in the tanyard and following them right down, where there was a loss of the non-tanning matters. That had been tried not only at their experimental yard, but at many others, and the non-tannins were not found to decrease in any appreciable quantity other than in the formation of acids, which were produced by natural fermentation. Mr. Cross had raised practically a new point in tanning. They had gradually had forced upon them in the last two or three years newer substances which, for want of a better name (and perhaps it was as good a name as any) they termed colloidal tans, and there was no doubt that some of the present ideas of tanning would have to be modified. There was no doubt that some of the tannins which Mr. Cross had been experimenting with recently had, if not a future before them, at least a very great interest, and it was a matter of interest to those engaged in the industry whether those products were going to find a niche in the tanning industry or not. Personally, he would welcome them if they produced a better leather than was produced at the present time. There was no doubt that the gallic acid, which was present in these extracts originally, was removed by means of gelatine, and the final detannization by means of hide powder. No one could deny that gallic acid did assist in tanning, but leather could not be made from gallic acid. Another unfortunate fact about gallic acid was that it actually dissolved leather, especially at the early stages. If the early liquors in a tanyard contained a high proportion of gallic acid they were actually going to dissolve a certain amount of leather-forming material and turn it down the drain. That was a matter the tannery chemist had to watch. He said that Dr. Rideal's criticisms were very pertinent as to what quality of leather was produced. He was afraid that he must refer Dr. Rideal to the previous paper, which was done on a practical scale with some tons of leather. In that case they had gone into the physical

Digitized by Google

tests very carefully, but in the case of the present experiments there were only some 400 or 500 grams of leather contained in each series; therefore it was not possible to carry out the physical tests. But from the ordinary judgment of the leather, they found that certainly the best leather, from the point of view of appearance, was produced from those solutions which contained the lower proportion of non-tannins. On the other hand, the color was better in those that contained the higher proportion of non-tans, but he thought that almost followed naturally. The importance of the subject was, perhaps, going to be greater with the introduction of the newer bodies, which were coming along very fast.

VALUE OF NON-TANS IN EXTRACTS.

A CRITICISM.

By H. C. Reed.

The foregoing article by Dr. J. Gordon Parker and J. R. Blockey, M. Sc., entitled "The Value of the Non-Tans in Tanning Materials and Extracts," seems to the writer to be to some extent misleading in the conclusions drawn.

The writer holds no brief for the advocates of high non-tannin extracts but claims that in the article referred to the authors have not given sufficient consideration to certain details which might tend to mar rather than to make the justness of the conclusions arrived at.

The criticism is mainly directed against the method pursued for determining the value of the non-tannins in the presence of acid, where the authors have added equivalent amounts of an acid suspender liquor to liquors made from a chestnut extract, without and with the addition of pure non-tan liquor. The purpose of adding the acid liquor was as affirmed, with the intent of paralleling tannery conditions and to offset the contention that the greater fermentation of liquors in the presence of higher proportions of non-tans would cause greater swelling of the pelt and ultimately heavier leather. But have the authors by the method pursued really proven their case? The addition of equivalent amounts of the acid liquor has acidified the solutions

Digitized by Google

to which it was added to the same degree. The claim of the advocates of high non-tans is, however, that the greater the non-tan content, the greater the amount of acid from fermentation, and the authors agree to the truth of this by submitting figures (p. 199, this issue) showing the higher acid content in the liquors in direct proportions to the amounts of added non-tans. Now since it is very evidently true that the liquors with the higher percentage of non-tans will ultimately give liquors of higher acidity and greater swelling effect, and the experiments were made with liquors of the *same* acidity and consequently the *same* swelling effect, the results do not necessarily show the true value of the non-tans. Or putting it in another form—should not the authors have shown results of experiments made with the tan solutions containing not only varying amounts of non-tans but also varying amounts of acids, the acidities being figured in the ratio of the non-tan contents of the solutions used or in the ratio of the acid-producing abilities of the solutions figured from the non-tan contents. Yet another point not thoroughly understandable to the writer is the fact that although the authors state that the leather was oiled in finishing no item appears in the analyses of the finished leathers which accounts for the oils contained, and yet the various items added amount to 100 per cent. in every instance.

The method pursued in tanning the pelts even when the suspender liquor was added would seem entirely to fail in even approximating tannery conditions in so far as the influence of the non-tans in their acid producing functions is concerned.

The writer further contends that it is eminently unfair to draw comparisons between the analyses of the leathers when they are not brought to an approximation at least of the same completeness of tannage. For example we find in the first table analyses showing in hide substance content respectively 42.6, 43.1 and 43.0 per cents., the degrees of tannage corresponding being 70.4, 67.5 and 67.2.

Comparing this with the analysis given in a later table we find in this hide substances of 48.1, 47.7 and 49.5 per cents. respectively with corresponding tannage degrees of 54.3, 55.8 and 50.9. There is a difference of 16.1, 11.7 and 16.3 in the degree of

Digitized by Google

tannages between these two tables with a maximum difference of but 3.2 between the items of the first table and 3.4 between the items in the second table. If in the second table cited the leather had been tanned to the degree shown in the first table it is not at all improbable that different results would have been obtained. This increase in the degree of tannage could have been gotten by extending the time of tannage, which would have tended to increase the acidity proportionally more in the higher non-tan liquors, which increase would have just as naturally resulted in a gain in the case of the leather tanned with these liquors. What impresses the writer particularly is that the authors of the article have so signally failed to prove their case from a practical point of view.

Referring to *Journal of the Society of Chemical Industry*, Vol. XXIX, No. 6, p. 315, we find a statement that the acidity of liquors, used in carrying on experiments to show the effect of high non-tan extract made by a pressure system of extraction in comparison with a low non-tan extract made by the open system, was carefully noted, but in no case was there any material difference, that the acidity of the liquors was measured each day and kept uniform throughout. These two statements are not altogether clear to the writer, but it would seem that if the "acidity of the liquors was kept uniform throughout" there could have certainly been no advantage allowed to the liquors made from the high non-tan extract, and the advantage that these liquors may have had over the low non-tan extract therefore nullified. In the reference above quoted the author states that the results "indicate that a high percentage of non-tans in an extract is of no advantage." As the authors of the more recent article (*Journal of the Society of Chemical Industry*, Vol. XXX, No. 24) say that "one influence of the non-tanning matters is in the production of acidity," and go on to give figures showing this, the writer fails to see the value of the conclusions reached that high non-tans have no advantage when the very advantage (increased acidity and consequent increased plumping ability) was not permitted them.

It might be claimed that in the tests made to prove the value of the non-tans (*Journal of the Society of Chemical Industry,*

Digitized by Google

Vol. XXIX, No. 6) that a sufficiency of acid was maintained throughout, and that even had the higher non-tan extract developed more acid and raised the total acidity of the liquors it could not have affected the results with a sufficiency of acid present. The writer claims that such a contention would be equivalent to avoiding the issue, which is not the value of the non-tans under conditions which do not permit the development of their value but their value under conditions which foster such development.

Even if it is granted that non-tans prevent the penetration of tan the writer fails to see that this has any particular bearing on the ultimate leather. On the contrary it is a well-established fact that too rapid penetration will give inferior leather and low gains. The experiments conducted (*Journal of the Society of Chemical Industry*, Vol. XXX, No. 24) to prove the influence of non-tans upon penetration, weight of leather and leather forming properties allowed a tanning period of but three weeks. It would have been interesting to have been favored with figures along identical lines with the period extended to three months and with liquors not complicated by the addition of other tanning materials. It might very easily be true that the low non-tan extract used in the tests would in the longer period of tanning show up inferior to the high non-tan extract, the leather in the latter instance being more open and permitting better penetration of tan to the interior during the later stages of tanning. The slower penetration of tan into the pelt assuredly does not of itself imply that the resultant leather will be in any way inferior or of less weight. Nor does it follow that if the tanning is done with extracts from the same raw material, one with low and the other with high non-tans, that the latter cannot be made to produce equal if not better weight and quality than the former. It is the contention that the authors in the articles referred to neglected to so parallel tannery conditions as to justify all the conclusions reached; that this neglect is evinced in the point of acidities, which will favor the high non-tan extract when sufficient time is allowed for full fermentation, and in point of time, which in the later work cited was not of sufficient duration to equal tannery conditions and to give to a slower penetrating material the benefit that the very fact of its slower penetration might have.

TANNING RESEARCH LABORATORY.

Digitized by Google

NOTES ON THE PLUMPING OF HIDES.

From the Bulletin of the Bourse aux Cuirs de Liége, Liége, Belgium, Feb. 4, 1912.

Hides may be plumped by the action of many substances, the most interesting being acids. Alkaline plumping is very injurious, as it causes the hide substance to be dissolved on the slightest increase of temperature and also renders it more susceptible to the action of micro-organisms. Under the influence of acids, the hide is also changed in character; its thickness is increased; from being opaque it becomes translucent and rigid with a peculiar "feel." A hide is considered sufficiently plumped when it shows a certain degree of transparency in daylight. Either too much or too little plumping are prejudicial to the leather. Both mineral and organic acids are used for plumping, sulphuric, hydrochloric, acetic, lactic and, more recently, formic and butyric acids being the ones chiefly used.

When a hide is sufficiently plumped it must be thoroughly washed in water; otherwise the strength of the fiber is weakened. Acids also produce dark lines in the spongy center of the hide, which absorb tannin and coloring matter in excess of other portions of the skin, and when these are attacked by the acid they burn and form dark inelastic lines under the grain and cause the latter to crack. This remark applies chiefly to mineral acids, although organic acids may produce the same results if the hide is insufficiently washed. Sulphuric acid has the special disadvantage of remaining in the hide even after the most careful washing, and eventually destroying the leather. The quantity of acid used must be very small and yet sufficient to neutralize all the alkali, and to prevent flatness from the tanning operations and too low a yield of finished leather. The quantity of acid used depends on the method of unhairing; skins unhaired with sulphur or lime are more sensitive than those treated by sweating. Plumping with acids is not adapted to the old system of tanning where weak liquors are used in the beginning. Numerous works have been published on plumping: Villon, Körner, Paessler and Sluyter have all published the results of their experiments.

The Tanning School of Liége, Belgium, has made recently a

Digitized by Google

comparative study of the plumping action of hydrochloric, acetic, lactic and butyric acids, and we give below the results obtained. Pieces of hide were immersed in weighed solutions of the different acids. After a few hours, those which had been put in hydrochloric and acetic acids were sufficiently plumped while those in lactic and butyric acid were still opaque. The latter were therefore left for 24 hours when they had become translucent. The quantity of acids absorbed by the hide was as follows:

	Weight of hide	Acid absorbed	Per cent. of acid absorbed to weight of hide
Hydrochloric	121.1	2.098	1.732
Acetic	117.5	4.200	3.57
Lactic	123.6	6.400	5.18
Butyric	126.8	3.03	2.4

These results show for the acids used, that the yield is large just in proportion to the smallness of the quantity of acid absorbed. The pieces of hide were then thoroughly washed to remove all traces of acid and then put into a 2 per cent. solution of formaldehyde. Körner has proved that the formaldehyde has not sufficient plumping action to be taken into account but does "fix" the plumping already obtained and prevents subsequent fermentation.

The pieces of skin so treated were then tanned in strong liquors made by mixing mimosa, quebracho and chestnut. After tanning, the skins were finished without the use of anything to give weight or improve the color. After finishing, we found that hydrochloric acid had produced the largest yield and that both acetic and butyric acids produced a larger yield than lactic acid. The finished leather from the hide plumped with acetic, lactic and butyric acids possessed a fine clear grain, while that plumped with hydrochloric acid gave a coarse, rough grain.

THE ANALYSIS OF TANNING EXTRACTS.

(*Le Cuir*, Vol. XXXVII, Jan. 15, 1912.)

A study comparing the official method by shaking and the old filter method as applied to certain cold soluble bisulphited quebracho extracts, undertaken upon the advice of the French Dyeing and Tanning Extracts Company, "Le Havre."

By Dr. E. Schell.

We have had to show on many occasions that certain cold soluble bisulphited extracts of quebracho present very great

Digitized by Google

difficulties to the official shake method in the matter of obtaining concordant results, at least approximately uniform results in the case of various laboratories in different countries. Dr. Parker has already officially referred to this at the time of the last meeting of the English Section (I. A. L. T. C.) at London, and we have gone to him personally for the purpose of comparing ourselves his manner of work with our own, and of attempting to determine the point or points which may be the cause of the divergence of these analyses. We will say at once that our methods of work are almost identical, and that the differences observed could not have their origin in the execution of the method. We are happy thus publicly to thank Dr. Parker for the courtesy which he showed us in permitting us to see on the spot his method of work.

We will give here a single example from many to demonstrate how much the results may vary.

	Prof. Dr. Procter	Dr. Parker powder Portway and Co.	Prof. Dr. Paessler Freiberg powder	Thuau powder Portway and Co.	C. F. powder Portway and Co. I	C. F. powder Portway and Co. II
Insoluble	0.04	0.0	0.4	0.0	0.0	0.0
Absorbable	35.94	36.3	39.9	37.6	37.1	36.0
Non-tannins	16.27	16.8	12.7	15.5	15.7	16.8
Water	47.75	46.9	47.0	46.9	47.2	47.2

Dr. Paessler has verified carefully his surprising result and has found it entirely confirmed. He attributes it to the use of the white Freiberg powder, which he chromed carefully for each analysis, following the directions of the official method. He has also assured us that he followed most scrupulously all the other official directions.

We have, on the other hand, no doubt that by agreeing rigorously to use the same hide powder, and perhaps the other reagents, concordant results might be obtained by this shake method, but we claim that the same would be true for the filter method, and that this matter alone does not suffice to distinguish which of the two methods better expresses the truth. The question standing thus, my company commissioned me to examine scientifically and practically which of the two methods responded better to what was known about the tannins of quebracho. The following lines give a brief review of my first researches in this direction.

Digitized by Google

We have chosen as a starting point a pure extract of quebracho, specially purified, of which we determined the analytical constants by analysis in duplicate by two different analysts in our laboratory of research. We give here only the mean results, but the original results are carefully preserved in our archives and we shall be happy to prove the absolute concordance between the various analyses in detail, as well for one method as for the other.

Here are the figures of the results on the pure quebracho which has served us as a point of beginning:

	Shake method American hide powder Portway and Co.		Filter method chromed hide powder Freiberg	
Density	25° Bé		25° Bé	
Insoluble	2.95	43.55	3.05	44.50
Absorbable	40.60		41.45	
Non-absorbable	5.40		4.65	
Water	51.05		50.85	

The extract thus carefully analytically determined was next transformed into a cold soluble product by bisulphiting, the proportion being rigorously maintained that 100 parts of the 25° extract are represented by 115.7 parts of the transformed extract, which was then analyzed in the multiple fashion described above and gave the following results:

	Shake	Filter
Density	30.2° Bé	30.2° Bé
Insoluble	0.0	0.0
Absorbable	36.0	41.65
Non-absorbable	14.5	8.85
Water	49.5	49.5

We will say at once that the conditions under which we performed the solubilization were such that no destruction of the tanning materials of the quebracho could have taken place. A very long practice with this product having familiarized us thoroughly with all its properties.

We must furthermore establish for this transformation a veritable tannin account, and we arrive at the following surprising results:

Examining the analytical results, we have the proportions as follows:

Digitized by Google

by the official shake method, $36 \times 115.7 = 41.65$ of tannin;

by the filter method, $41.65 \times 115.7 = 48.18$ of tannin;

so that we shall have respectively,

by the shake method, 43.55 available;

by the filter method, 44.50 available.

According to these figures, it appears *a priori* most surprising that the official shake method shows a loss of tannin which appears to be in a certain proportion to the opposing gain which results from the filter method. On the basis of the studies which follow, we are justified in giving the following explanation for the special case of bisulphited quebracho extract which we are studying. We have begun by submitting a fundamental study of the non-tannin solutions corresponding to the above analyses and have found the following surprising results:

	Non-tannins by the official shake method—American hide powder from Portway & Co.	Non-tannins by the filter method—chromed hide powder from Freiberg
1. Saponification by dilute sulphuric acid.....	Brownish green coloration	Colorless
2. *a*—Addition of iron alum *b*—Addition of iron alum and acetate of soda	Olive green coloration Wine color	Colorless At first colorless, then precipitation of hydrate of iron.
3. Treatment with formaldehyde and hydrochloric acid	Intense reddish brown coloration, with pink froth; after cooling and standing, a considerable brown precipitate	Colorless, after a certain time of standing, a very slight colorless precipitate.
4. Kiliani's reagent.....	Very distinct reaction of tannate of phloroglucin	Absence of reaction.

All these non-tannin solutions, in spite of the above differences, showed themselves perfectly detannized by the usual gelatine reagents. It clearly appears therefore, that the shake method has not absorbed certain substances which give tannin reactions, which, on the contrary, are shown (as tannin, tr.) by the filter method.

One of us, Dr. R. Lepetit, has proved and published some years since that in the treatment of extracts of quebracho with bisul-

Digitized by Google

phite, there is not only solubilization by the formation of an unstable bisulphitic compound, but that at the same time occurs the formation of real sulpho-linked organic compounds. By this demonstration of Dr. Lepetit, that is to say, the formation of genuine organic compounds between the tannin of the quebracho and the bisulphite, the molecule of quebracho tannin increases in size, because of the sulpho-linked grouping, and in consequence a part of the bisulphite used ought to disappear from the array of non-tannins, and appear among the tannins, which is precisely what takes place in the filter method, while on the contrary, the shake method shows a corresponding loss.

It cannot be surprising in the case of such sulpho-linked organic compounds that they do not retain the original properties of the mother substance so completely as, for instance, not to have lost certain precipitation reactions in consequence of this sulphonation, while, however, they have preserved unchanged the characteristics which depend on the hydroxyl groups within the molecule retaining their positions unchanged. But we are forced to add that not only are these last reactions preserved, but also in particular, the property *of being absorbed by hide under certain conditions*. For, in spite of the fact that this does not take place in the shake method, where the contact of the tannin solution with the hide powder is very brief (and perhaps sufficient for a non-sulphonated tannin), this absorption takes place, without doubt, in the filter method, where the time and the conditions of contact of the two reacting substances are entirely different.

It appears indeed extremely probable that in the case of practical tannage where the time is much longer and where the hide behaves like a filtering diaphragm, this absorption takes place according to the filter method rather than according to the shake method. It may further be considered that it is just these transformed tannins that contribute to rapid penetration and are for this reason very useful.

We have also, it must be said, varied our conditions of work in diminishing the formation of sulpho-linked compounds, and have been able thus to reduce the difference between filter and shake methods, so that for example, with the same original extract mentioned above, 38 per cent. is opposed to about 40.5 per cent.,

Digitized by Google

and we have made the following curious observation: the approach of the two methods is not made from one side; that is to say, one of the two methods does not approach the other, while that one remains unchanged, but each of the two methods gives results nearer the mean of those given above for the two on the bisulphited extract, which fact constitutes a new proof of that which we have announced above.

In all the cases which we have studied, the non-tannins of the shake method show very distinct tannin reactions, which are completely lacking in those of the filter method.

We particularly suggest to any of our colleagues who may wish to collaborate in this study, not to lose sight of the comparative study of the non-tannins, of which we have spoken above.

In accordance with all this which we have said, the official shake method therefore does not appear to represent the chemical conclusions in that which concerns certain sulphited quebracho extracts, and we shall continue our researches in this matter, but we propose in the meanwhile to restore again to the old filter method the place which belongs to it, in default of a better.

DR. E. SCHELL,
Member of the Commission on Analysis of the French Section of the I. A. L. T. C.

ABSTRACTS.

Splitting Leather with a Band-knife Machine. *Leather*, 3, 773-4, 877-8, 957-8, and 4, 26-7. Satisfactory splitting can only be done when the stock is in proper condition. The leather should lie in pile at least 24 hours beforehand. Some manufacturers split the hides in raw pelt. This is hard on the machine and does not give such uniform results as splitting when half or fully tanned. For chrome tannage it is necessary to split from the limes, but when such splits are bark-tanned, the thickness of the leather will vary, although the hide splits are fairly uniform in thickness. Knives are said by some operators to last longer in splitting half-tanned skins, and the speed may be greater than when fully-tanned goods are split. Hides for splitting are best "sammed" by machine ("pressing"), as the process is much more rapid, and the leather after jacking comes to the splitting machine in more uniform condition. In re-splitting hides after full tanning, great care is necessary in dampening, to use just the right quantity of water, which is best applied with a brush. The splits are then folded and lie piled for 24 hours before re-splitting.

Digitized by Google

(NOTE.—The band-knife working on stock fully tanned always causes "sucks" and low spots in the grain.)

Before attempting to split with a machine, it is well to overhaul it. The first thing to do when overhauling a machine is to take the knife off, then slide the bottom knife jaw back as far as possible without taking it out; this will enable you to see whether the outlet, or section plate, is true or not. If this plate is worn on the faced side, it is advisable to have it planed. Unless this is seen to, the section roller will not lie level. Examine the ends of the outlet plate to see if they fit tight in the V plates. It is these two small V plates which determine the exact position of the outlet plate and also the section roller. The center of the section roller, when placed close up to the knife, should be in a line with the top of the groove in the V plate. The bottom knife jaw can now be moved back into its proper position, gauging the distance from the center according to the class of goods to be split. The knife can now be put on, and the top knife jaw placed in position, when everything is ready for setting up. When setting the knife jaws, some men screw the jaws down just as they are, being satisfied so long as the knife is firm but free. This is a grave error, and is often the cause of much unnecessary labor. The correct method is, first to lower all the screws on the bottom jaw until the rings are level with the surface. This allows the top jaw to lie flat on the knife. Set up from this position, tilting the top jaw as little as possible. If the top jaw is set at too great an angle, the setting-up plates are liable to get wedged between the knife and the bottom jaw, thus causing the knife to bind, and in the majority of cases causing considerable damage to the surface of the knife and the jaws. The knife should be firm but free when set. Any play existing between the cutting edge of the knife and the jaws will cause uneven splitting. The substance or feed roller will also need examining to see if it sets accurately, and the small support rollers to be sure they work freely. The quickest and easiest method is, first to lift up the bridge as far as it will go by means of the wheels at each end, remove the plates at each end of the bridge and then remove the plates at each side of the substance roller. It is then an easy matter to ascertain whether the roller is true by the aid of a scribing block. The support rollers should also be cleaned well. Dirt and grease cause them to choke, and they will not revolve freely. When one of these rollers is choked with dirt, the action of the substance roller working against it grinds a flat about ⅛ inch wide on the surface of the support roller, and, unless the roller is sent to the engineering shop to be turned, it will leave the effects on the leather when split. When setting the plates which keep the substance roller in position, set the plates in the front of the roller first. This simplifies the setting of the back plate. The distance between the edge of the plates and the roller should be about the thickness of a piece of paper. Too much play causes a strain on the roller spindle.

The grinders will also perhaps need overhauling, and, if the emery

Digitized by Google

stones are very small, it is advisable to put new ones on. It is impossible to grind and keep a keen edge with small emery stones. Care should be taken to get the stones exactly true in the first place. The centers of the stones are not always true, and it may be found necessary to insert a little packing between the flanges and the stone to get them accurate. A stone which does not run true will always grind an uneven edge on the knife. The emery spindle, if a little slack, will also cause the stone to grind unevenly. Before setting up the small jaws which hold the knife in position for grinding, see if the bottom jaw is level with the knife. The knife should lie flat on the bottom jaw, and the top jaw should be screwed down as flat as possible to prevent any particles of emery getting between the knife and the jaw. As shown in the illustration No. 1, the cutting edge of the knife A should be set a short

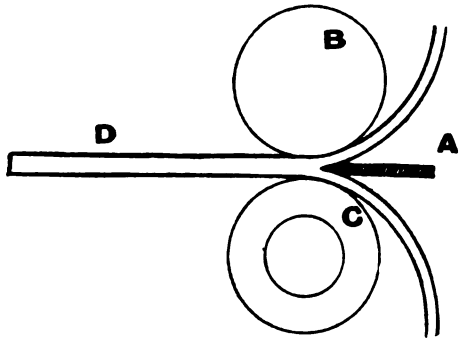


Fig. 1.

distance away from the center of the feed rollers B and C. the distance being gauged according to the thickness of the leather to be split. In this illustration it will be seen that the knife is cutting where the leather is firm, but where it has very little pressure from the rollers. If the knife was set nearer the center of the feed rollers, the pressure would be greater, too great, in fact, to allow of the free passage of the knife through the leather. This would cause what splitters generally term "binding" or "choking." One simple method of telling whether the knife is set too close to the center of the rollers, and one which never fails, is to split a thin shaving from a small piece of leather and then to examine the cut side of the leather. If the knife is set too close, the cut side of the leather will be a shade darker in color and very glossy. On the other hand, if the knife edge is set too far back, as shown in the second illustration, the leather would be very uneven when split. In the case of hides, where the bellies are always lighter than the butts, we should find that the cutting would be very irregular, and in some places, where the shanks were very light, the knife would have scooped pieces out, leaving holes. This is owing to the leather having nothing to

Digitized by Google

support and keep it firm while the knife is cutting. When splitting thin leather, the knife needs setting nearer the center of the feed rollers than when splitting thicker goods.

If a lot of leather of various thicknesses is to be split, in the first place sort them into three lots, *viz.*, light, medium and heavy. Then set the knife for splitting the light ones. By the time these are split, the knife, owing to the constant grinding, will be a shade further away from the center of the rollers, and in position for splitting those of medium thickness, and the same applies to the heavy ones. Always set the knife for splitting the lightest, then follow with the medium and the heavy.

The right bevel to use depends mostly on the tannage and condition of the leather. If the leather is all of one tannage, one particular bevel will do for all classes of work. If different lots of leather are to be split

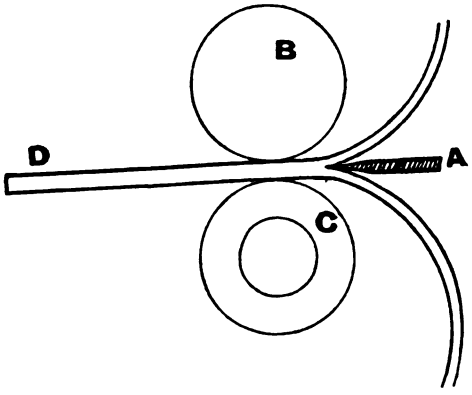


Fig. 2.

of different tannages, as is often the case when splitting for a leather dresser, either particular care must be taken that the different tannages are sent to the machine all in the same condition, so that one kind of bevel will do for all, or the different tannages may be taken as they come, and the bevel ground accordingly.

It is necessary at times, especially when splitting English hard tanned leather, to grind a very small bevel before it is possible to get a clean easy cut. But this kind of bevel would not always prove satisfactory on all classes of leather. No. 3 is an illustration of a knife edge which will give good results on nearly any class of work. The width of the top bevel is 3-16ths, whilst the width of the inside bevel is 7-32nds. When grinding this bevel, the bottom emery stone should be allowed to grind lighter than the top one. This will bring the cutting edge a fraction above the center of the thickness of the knife. A larger bevel on the inside of the knife facilitates the passage of the split, which is often

Digitized by Google

many times thicker than the leather passing over the top bevel. This method always gives a nice clean cutting edge.

When grinding, it is advisable not to have the stones on too heavy. If you examine the knife edge after a heavy grind, you will find that minute particles of the edge have broken away, leaving the edge rather like a miniature saw. This should be avoided whenever possible. If it is impossible to keep a keen edge when splitting without grinding heavy, it is a sure sign that the knives you are using are not tempered hard enough for your class of work. The best thing to do is to try a harder tempered knife. For fully tanned hides it is advisable to use an oil-tempered knife; they are a little more expensive than the ordinary knife; but they do not wear away so quickly, and it is possible to keep a keen edge on these knives when splitting very hard leather, without excessive grinding.

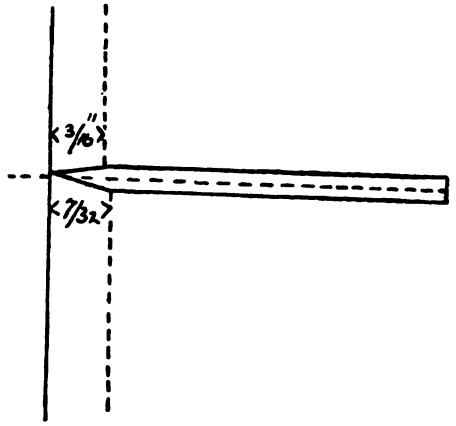


Fig. 3.

There has been a great improvement in the manufacture of band knives during late years, the quality of the steel, the brazing and finishing having greatly improved. The knives now in use very rarely break or crack. I have used one make of medium knives for the last four years, and have not found a fault with any one during that period. Of course much depends upon the handling and subsequent care of the knife. Great care should be taken when removing a knife from a crate and putting it on the machine. It should be kept perfectly straight to prevent the back edge being strained, as even a slight twist often makes it run unevenly in the machine. The knife should also be well cleaned before putting on the machine, and every particle of rust and dirt carefully removed from both sides. Dirt between the knife and the jaws may cause the knife to bind, doing damage to the knife and the jaws, besides causing unnecessary labor. When setting up the knife wheels care should be taken not to pull the knife too tight. It will run evenly in the machine, if the wheels are true, without having it too tight. Too much strain upon the

Digitized by Google

knife will also cause it to run warm. Again, a tight knife affects the brass screw bushes of the knife wheels, wearing away one side and making it difficult to set the wheels accurately. When setting the knife wheels use a line. The line is stretched tight across the center of the two wheels and allowed to lie flat on the surface of the two outside flanges. then by manipulating the screws on the two slide brackets the inside flanges can be brought into line with the outside flanges. This will bring both wheels true. After setting the knife jaws the knife, if set accurately, should be quite easy to turn by hand. Any resistance will either be caused by the knife being pulled out too tight, or by being set too tight in the jaws. The knife wheels should be cleaned regularly every day. Much dirt and grease accumulates on the surface of these wheels during a day's work, and is often the cause of the knife skidding on the driving wheel.

The knife should be well cleaned and lubricated. The cleaners should be changed at least three times a day, and a little paraffin should be added to the oil used on the cleaners. If dirty cleaners are allowed to stay in the machine the knife, instead of being cleaned and lubricated, carries the particles of dirt and emery into the jaws. When work on the machine is finished each day, the knife should be allowed to run for a few minutes between cleaners soaked in paraffin; the cleaners are then changed and the knife allowed to run between dry cleaners. The paraffin cleans out any dirt and thick oil which may have accumulated between the jaws. Before leaving the machine at night, see that the braze of the knife is on the flat and not on the wheels, as if the joint is left on the bend it is liable to break away. The knife also should be slackened off a little, as it sometimes becomes warm and expands, but on cooling contracts again. This is noticeable when the machine has been standing a few minutes by the continued clicking of the knife caused by contraction. In winter time, if the splitting machine is in a very open place, cover the knife up with canvas when not in use, as a severe frost may cause a knife to crack.

Much depends upon the condition of the rubber roller, and there is one important thing to remember, viz., that oil or any kind of grease will ruin the rubber. There are a few pure rubber rollers in use to-day, but most of them are made of some composition. The pure rubber rollers are softer and more pliant than the composition rollers, and are the most suitable for hide splitting. If the rings of the section roller cut into the rubber, the sharp edge should be removed with a smooth file.

To preserve the surface of the rubber roller, have two extra rings made for the section roller, one a little wider than the standard size, and one a little less; the combined width of these two rings to be the same as the width of two ordinary rings. These should be substituted for two of the ordinary rings on the section roller. By altering the position of these two rings it is now possible to alter the pitch of all the other rings on the roller, and this prevents the rings cutting into the rubber so much. These rings should be altered every few weeks; if this is done the rubber roller will always have a nice even surface. If the

Digitized by Google

rubber roller is very hard it should be smeared over with flowers of sulphur mixed to a thick paste two or three times every week. If this process is continued the rubber will gradually become softer and more pliant. On some kinds of work, especially leather of a greasy nature, the rubber becomes so greasy that it will not grip the surface of the section roller, and it is only with the greatest difficulty that the leather will feed at all. A rubber roller in this condition should be washed every night with a strong solution of soda applied with a brush while the roller is working. The section roller should also be well cleaned with paraffin. The best plan is to pour a little on the section roller, then work the rings about; this enables the paraffin to penetrate between the rings, and remove any dirt. When a rubber roller needs levelling, send it to the makers. The roller is removed by grinding, which is the most economical method.

Often when splitting hides or kips—especially light and medium weights —it is a difficult matter to prevent nipping the shanks. This generally occurs in the hind shanks where the leather is very thin. Sometimes it is in the form of a narrow groove, only the light grain being left. so thin that it is possible to see through it. It is only by careful setting of the machine and careful feeding that this can be remedied. The difference in the thickness of a hide at the butt and the weak part of the shank is the main cause of the trouble. It is necessary to have a good rubber roller to thoroughly master this defect. The rubber should be pliant enough to allow the rings of the section roller to sink freely without putting any great strain on the rollers, as it is when the rubber is too hard that the section roller drops. The pressure of the section roller when feeding forces the rubber roller outwards, thus increasing the space between the rubber roller and the outlet or section plate and allowing the section roller to fall away from the knife. No matter how tight up the small support roller may be, it will not prevent the section roller falling away if the rubber is hard. The section roller forces the rubber roller outwards, and not as the position of the support roller would suggest, downwards. The knife should be set as near the center of the feed rollers as it is possible to work, and the section roller should be set close to the knife edge, but not touching. When feeding care should be taken to keep the thin part of the shank tight when entering between the rollers. Those working at the back of the machine should be instructed to hold the hide up tight, this prevents the very thin parts of the hide touching the knife, and those who have never bothered about holding the leather up as it comes out of the machine are recommended to try it. It is surprising the difference it makes, especially on light work. Part of the split sometimes becomes trapped between the section roller and the outlet plate. On some machines this occurs very often and causes the operator much trouble. This trapping of the split can be traced to two sources: first, the front plate which keeps the section roller in position may be responsible, or it may be due to the condition of the outlet plate. If the front plate, or "feed plate," is not set well up to the section roller the

Digitized by Google

leather, when passing through the machine, will force the section roller forward, leaving a space between the section roller and the outlet plate sufficient to allow of the passage of a thin piece of split between them. To remedy this the front plate should be set closer to the roller; when setting, the front edge of the plate should be lowered by means of the screws provided for the purpose, until the plate fits snug against the roller without binding in any way. The top of the groove on the front edge of the plate should be touching the roller. This prevents any of the rings on the section roller jumping up and catching the knife edge. Sometimes, even when the front plate has been set as it should be, the split still finds a way between the section roller and the outlet plate.

The top edge of the outlet plate should be in line with the center of the section roller, as shown in fig. 4. In one case of this trouble it was found that the top edge of the outlet plate was a little above the center of the section roller. When the pressure of the leather forced the rings of the section roller down it left enough space to allow the split to pass

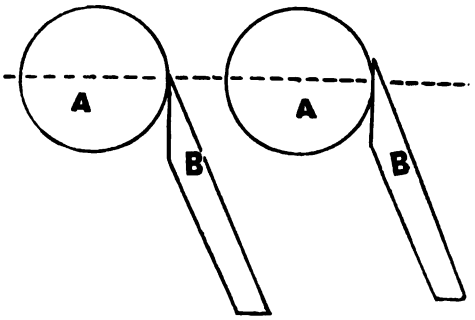


Fig. 4.

between the back of the roller and the edge of the plate. This was owing to carelessness in the making of the machine. The edge of the outlet plate was lowered until it was in line with the center of the section roller; packing had to be inserted at each end between the back side of the plate and the inside of the V-plate to prevent it moving. Since this was done the machine is doing excellent work. Sometimes the setting-up plates cause trouble by becoming wedged between the back edge of the knife and the bottom jaw. This is caused by the top jaw being set at too great an angle. It should be set as flat as possible, care being taken not to bind any of the setting-up plates. It is always advisable to use a strip of steel between the setting-up plates and the knife. They are about half an inch wide and the same thickness as the knife, and can be had of any maker of splitting machines.

Section roller marks are generally noticed when splitting very thin, and it is often very difficult to prevent them without causing other damage to the leather. The fault is due to the space which exists between

Digitized by Google

each of the rings on the section roller. In the first place it is necessary that a little space should exist between each of the rings, or the rings would not rise and fall freely. A certain amount of play is needed if the rings are to work independent of each other. The only thing possible to do when using an ordinary section roller is to prevent the rings having too much play. The roller should be taken to pieces as often as possible and each ring thoroughly cleaned, particular notice being taken of the sides of each ring to see that they are perfectly smooth. If this is done regularly it will be found that the rings will work freely with very little play. If the roller is neglected and dirt allowed to accumulate between the rings, they will bind and perhaps cause damage to the leather. Having the section roller too tight on light work is perhaps worse than having it too slack; in this case, if one of the rings sticks it often results in a hole being made in the leather the width of the ring, which destroys the leather for the purpose for which it was intended. A new roller has been put on the market which entirely eliminates the ring marks frequently caused by the old section roller. It is specially adapted for very light work and gives excellent results when buffing. This roller consists of a spiral-wound brass wire and is positively driven, the end of the roller being fixed in a revolving collar which is attached to the cheek at the loose end of the machine. which in turn is geared to the end of the spindle of the rubber roller. This greatly facilitates the feeding of the leather in the machine. This roller has been in practical use in America for a number of years, but has only recently been introduced in England. There are also special grinding stones, which work independently of the ordinary emery stone, and produce an exceptionally fine edge on the knife. with the result that the cut is very fine indeed. The general tone of the splitting is greatly improved by the use of this new roller and the new grinding stones.

New Studies on the Tanning of Gelatine and Hide. L. MEUNIER and A. SEYEWETZ. *Collegium,* **1911,** 373-9. A uniform quality of gelatine in thin leaves was used. This was cut into small strips and 10 gr. placed in a wide-mouthed bottle with 500 cc. of insolubilizing solution. Every 15 minutes a sample was taken out and tested with boiling water. *Gaseous Cl,* even in the absence of light, decomposed the gelatine without rendering it insoluble. *Chlorine water* alone, at temperatures from 15°-20° C. (60°-68° F.) did not render the gelatine insoluble, since the swelling and hydrolysis due to the HCl formed by the action of Cl on water in the presence of organic matter decomposed the gelatine. The addition of salt and lowering the temperature check the swelling and hydrolysis and permit the chlorine to render the gelatine insoluble. To 500 cc. of Cl water (saturated) and 10 gr. gelatine were added 50 gr. salt, and the temperature kept at about the freezing point. The absence of light helps but little. *Sodium hypochlorite* solution rapidly and easily renders the gelatine insoluble at temperatures from 10°-12° C. (50°-

Digitized by Google

54° F.). At higher temperatures the gelatine swells notably and the insolubilization is not complete. The addition of 2 cc. HCl to the 500 cc. of solution hastened the insolubilization, which is then complete in half an hour or less, the time without the acid being 1 hour. *Chloride of lime* produced results similar to those of sodium hypochlorite. In this case rise of temperature is more injurious. Good results were obtained up to 10° C. To the 500 cc. of solution 20 gr. chloride of lime were used, and good results were secured with 100 gr. salt or with 2 cc. HCl instead of the salt. The gelatine retains an excess of Cl very tenaciously. After washing in running water 12 hours, 15 minutes soaking in a 10 per cent. solution of commercial bisulphite, and a further washing in running water for 2 hours, it was washed in alcohol and dried. Analysis then showed 0.26 per cent. Cl in the dry gelatine insolubilized by sodium hypochlorite, and 0.35 per cent. in that treated with chloride of lime. *Bromine water* rapidly renders gelatine insoluble without decomposing it. Swelling due to HBr is avoided by the use of salt. To 400 cc. of water, 100 cc. of saturated Br water and 100 gr. salt were added to treat 10 gr. gelatine. The best temperature is from 10° to 12° C., and the time required ½ hour. *Sodium hypobromite.* To 400 cc. water add 100 cc. saturated Br water and just enough soda to saturate the Br. No salt is necessary. Results similar to those of Br water. The treated gelatine was washed as in the case of that treated with Cl and analyzed. The percentage of Br retained is about 0.9 as in the case of hide. (See Abstract, this JOURNAL, VI, 528). *Iodine* and its compounds do not render gelatine insoluble. The effect of halogens on hide is similar to that on gelatine, the best results being given by bromine, as described in the abstract referred to above. The authors suggest that treatment with Cl or Br may be used (1) to preserve white hide and (2) as a fore-tannage for all varieties of hides and skins. A practical solution for the first purpose is made by taking 75 gallons of water for 200 pounds hide and adding 6 pounds chloride of lime and 6 pounds salt. One hour's treatment with frequent agitation suffices for sheep skins. Skins so treated may be tanned in any manner, suffering no disadvantage from this preliminary tannage, and in many cases making better leather than similar hides tanned immediately after being taken off. L. B.

Notes on Neats-foot Oil. W. FAHRION. *Collegium,* **1911,** 209-212. Neats-foot oil is specially valuable for two properties, it does not easily become rancid, and resists the action of the oxygen of the air, and it solidifies at a very low temperature. Because of its high price, adulteration of neats-foot oil with even a small percentage of cheap oils is profitable, and such adulteration is no doubt frequent. Little has been done toward methods of detecting such adulteration. Neats-foot oil is prepared not only from the hoofs of cattle, but also those of sheep, pigs and horses, and the chemical character of all these is very similar. Refined bone oil seems also to be closely related. Actual adulteration commonly

Digitized by Google

involves vegetable oils, especially rape and cotton-seed. Constants of neats-foot oil as given in the books are: Acid value, 1.5-7; Saponification value, 189-199; Hehner's number, 95.2-95.5; Iodine value, 65-78; Melting point of fatty acids, 28-31° C. Fahrion examined 11 samples of neats-foot oil and 5 of bone oil with results as follows:

		Acid value	Saponification value	Iodine value	Melting-point of fatty acids	Mean mol. wt. of fatty acids
Neats-foot Oil	1	9.0	197.6	85.2	28°	279.8
	2	2.7	195.8	68.5	29	276.1
	3	4.7	197.3	59.7	37	280.0
	4	2.4	193.4	71.5	29	283.5
	5	6.8	196.1	64.3	34	275.4
	6	6.6	190.3	76.5	30	286.8
	7	4.0	189.0	76.7	26	284.6
	8	2.5	190.8	81.8	21	284.8
	9	10.0	195.3	84.5	25	280.3
	10	7.6	192.0	64.9	30-31	279.4
	11	3.7	189.9	82.6	23	288.6
Bone Oil	1	9.0	196.1	74.2	34	279.5
	2	3.8	191.3	67.4	28-29	280.8
	3	2.4	190.3	79.6	14	284.7
	4	6.2	186.7	79.8	21	294.8
	5	4.2	192.5	79.0	13	279.0

In 4 cases the acid value is above 7, implying low resistance to cold. A good neats-foot oil should be nearly neutral. F. believes the limit for acid value should be 6, corresponding to 3 per cent. free fatty acids. The saponification value lies within the limits excepting bone oil 4, which is evidently adulterated with rape. Suspicion falls on the 7 samples whose iodine value is above 78. Holde and Stange found that neats-foot oils whose iodine values ranged from 78.3 to 85 were adulterated. In 3 cases the melting point of the fatty acids is high, and this is doubtless due to adulteration. In 6 cases it is low, and this F. considers a favorable fact since it points to high cold-resisting power. From various data F. concludes that the mean mol. wt. of the fatty acids should not exceed 284, and he believes that the 3 samples which are above 285 are adulterated with rape oil. Holde and Stange (*J. S. C. I.*, **22**, 775) tested neats-foot oil for vegetable oils by separating the unsaponifiable matter from a large quantity of oil, crystallizing it from absolute alcohol and examining the crystal forms and finding the melting point. The pure oil afforded cholesterin in rhombic tablets with a melting point 145-148° C., while the adulterated sample showed needle-shaped crystals of phytosterin, melting at 130°. This method is troublesome. The author published some years ago a convenient method, determining the amount of solid fatty acids present and their iodine value. This method was applied to

Digitized by Google

some of the before mentioned oils, with results as below. No. 1 is clearly adulterated.

		Per cent. solid fatty acids	Iodine value	
			Solid fatty acids	Liquid fatty acids
Neats-foot Oil	1	20.6	13.1	105.4
	8	14.0	25.0	94.9
	11	14.0	19.7	96.9
Bone Oil	3	13.2	——	92.7

The Use of Chrome Leather in the Valuation of Tanning Extracts. G GRASSER. *Collegium*, 1911, 390-92. The use of the tintometer in determining the color of extracts is not satisfactory and is decreasing. White hide because of variation in thickness, etc., does not give uniform results, and lime in the hide causes darkening of the leather. If the hide is delimed with acid the acid is difficult to wash out, and if any remains it causes a notable precipitation of tannin and "reds," which results in poor tannage, and in change of color on the surface. If a number of pieces are delimed, it is difficult to preserve them, since phenol and $HgCl_2$ cause spots due to their tanning action, and formaldehyde also injures the hide. Splits are unsatisfactory because of their rough surface, and they give a darker color than grain. Gansser's "animalized cotton" serves not only to compare colors, but weight-giving properties, etc. Expensive apparatus is necessary to prepare and use it. The author has employed chrome leather for color tests with good results. Twenty-five gr. liquid or 8 gr. solid extract are dissolved in 100 c.c. water at 70° C., cooled, placed in a flask of 150-180 cc. capacity and shaken for an hour with a piece of chrome-tanned calf leather about 8 x 10 cm. in size and weighing about 10 grams. After lying in the dark for 3 hours the piece of retanned leather is well washed. After wiping with a clean cloth the pieces are air dried in the dark. The combination tanned piece gives the color due to the extract uninfluenced in shade by the original green color of the chrome leather, except when the extract is a very light one and is used in dilute solution. In comparisons, the quantities of extract used should be such as to give equal amounts of tannin in the test flask. The author notes that the hide-powder method of detannization shows a proportion of tannin greater than can be utilized in actual tanning, since while a new tan solution treated with hide powder yields colorless non-tans, one which has been used gives more color in the non-tans because of the higher percentage of non-tans in the liquor. The fact that a piece of actual hide will not take all the tannin from a solution plays an important part in the valuation of extracts, and it seems that the principal role in the color character of an extract is played not by the quantity and kind of non-tans but by the proper color of the tannin itself.

The Production of Leather and Fur which will Resist Treatment with Boiling Water. J. SCHNEIDER and V. SIMACEK. *Collegium*, 1911, 368-9.

Digitized by Google

Many dyes for leather work better at the boiling temperature, and for this reason a greater assortment of colors can be applied to chrome leather than to other sorts. Samples of leather were tested by treating them with hot water for a longer or shorter time and examining the water for gelatine. White hide was shaken and digested with boiling water and metallic salts with results as follows: (1) Reduced to glue, with salts of Be, Ca, Zn, Fi, V, Sb, Bi, Mn, Fe, Co. (2) Hide rendered soft and translucent, solution "jellied," salts of Cu, Rb, Ni, Os. (3) Hide tough, solution jellied, salts of Mg, Sr, Cd. Ba, Al, Zr, Sn, Pb, Mo, W, Se, Ru. (4) Hide tough, solution not jellied, but precipitated by tannin, Hg, Tl, Ce, Th. (5) Solution gave no precipitate with tannin, Cs, V, Cr, U, Pt. A few organic compounds were tried. To class (2) belonged beta-naphthol; to (3), benzaldehyde, thymol, alpha-naphthol; to (4), chloralhydrate, resorcin; to (5), formaldehyde, acetone, hydrochinon, phloroglucin. The behavior of the salts was influenced by their dissociation constant, by the kind of acid, by the acidity or alkalinity of the solution. Insoluble organic materials were dissolved in alcohol and the solution diluted with water.

European Wool and Leather Grease. CONSUL-GENERAL FRANK D. HILL, Frankfort. *Consular Reports,* March 1, 1912. Degras is obtained partly by scraping "chamois" leather with a knife and partly by washing it with alkali and then neutralizing the alkali with sulphuric acid. A French method presses the oil out of the leather under water, that so obtained being called moellon. The demand for degras is so great that at some tanneries inferior skins are worked over and over for the sake of the degras. Artificial degras is a mixture of moellon and artificially oxidized oil, or oleic acid and oxidized oil, sometimes with the addition of talc. In one German process the oxidization is effected by means of a ferment. Wool grease is washed out of the wool with soap and separated from the soap solution by a centrifuge. It is sometimes dissolved out of the wool with ether, etc. It has a disagreeable odor and is brown or yellow. Its sp. gr. is about 0.937 and it melts at from 102° to 108° F. It consists chiefly of cholesterin, and esters of the fatty acids. Distillation yields a mixture of cholesterin and free fatty acids, called wool oil or distilled wool grease. The crude grease is worth about 3 cents a pound. It may be purified by extraction with acetone or benzine or by "salting out." Treatment with alkali removes the fatty acids, forming soaps which may be dissolved out. The residue, containing 25 per cent. water, known as "lanolin," is used in the preparation of ointments, because it is readily absorbed by the skin.

CONSUL A. E. INGRAM, Bradford, Eng. Wool is washed in large vats with warm water, soap and alkali. The wash water was formerly run to waste. This has been prohibited by law, the enforcement of which in the West Riding of Yorkshire devolves on a Rivers Board. (See J. A. S. Morrison's article, this JOURNAL, Dec., 1911.) Many manufacturers are

Digitized by Google

now deriving a good profit from the purification of effluents to which they have been forced by law to resort. The city of Bradford permits manufacturers to run their waste into the sewers, and derives a large income from the wool grease recovered by the city plant in which the sewage is treated. Last year $122,000 profit was realized by the city and improved methods are being installed which will increase the income. The old method is as follows: The water is run into a large tank where it is treated with sulphuric acid, which breaks up the soaps and frees the grease. The whole is then run into a second tank having a filter bottom through which the water and soluble matters drain off. The residue is then scraped up, put into canvas packages, heated and pressed. The crude wool grease is thus extracted and the residue burned or used for fertilizer. A newer process which pays well where large quantities of wool are treated concentrates the waste to about one-twelfth of its original volume and separates the alkaline liquor from the fat emulsion by centrifuging. The alkaline liquors are then evaporated to dryness and calcined to destroy organic matter, when the salts are purified by crystallization. Wool grease is sold in 3 grades, the two lower averaging about $38 per ton. The highest grade sells at from $58 to $63 per ton, its price depending somewhat on the price of tallow. The cake left after extraction of grease is sold at from $1.50 to $2 per ton. Refiners obtain from wool grease a product sold as stearin, used in soap-making and leather-dressing; and "wool oil," which is used in the shoddy manufacturing districts with other oils for oiling wool. The residue from the refining process is known as wool pitch, and is used, among other purposes, as an electric insulating material.

A Method of Measuring Absolute Viscosity. HAROLD P. GURNEY. *Jour. Am. Chem. Soc.*, 34, 24-8, Jan., 1912. (Since in laboratory practice viscosity is usually measured simply in seconds, the type of viscosimeter being stated, it may not be out of place to preface our abstract of Mr. Gurney's article with a definition of "absolute" viscosity: The coefficient of viscosity is the force (in dynes) required to move a layer of the liquid 1 square centimeter in area past another similar layer 1 centimeter away, at the rate of 1 cm. per second. The value of this coefficient for pure water at 15° C. (65.5° F.) is 0.0134. The fluidity of a liquid is obtained by dividing the viscosity into 1, the two things being pretty closely analogous to electrical resistivity and conductivity.) Mr. Gurney claims for his method, accuracy and rapidity, and that it requires little time and labor to set up and calibrate the apparatus. The amount of liquid required is small. A capillary tube 1 meter long is held in a vertical position, dipping into a vessel of the liquid so far that a column of liquid 2 cm. long stands in the tube when undisturbed. Marks are placed on the tube 28.5 cm. above and the same distance below its middle point. Suction is applied at the top of the capillary until the liquid rises above the upper mark. When the air is admitted the column falls. By means of

Digitized by Google

a stop-watch the time of fall between the marks is observed. The author works out a formula, showing that the absolute viscosity (μ) of a liquid whose density is γ and which requires T seconds to fall between the marks spaced as above on a tube whose diameter is 0.695 mm. is given by the equation $\mu = 0.00247\ \gamma\ T$. The coefficient 0.00247 varies with the square of the diameter of the capillary, so that for a tube of twice the given diameter, this factor would be 0.00988. A jacket may be placed around the capillary through which hot water or steam may pass. A column is then drawn up and held until it acquires the temperature of the surrounding liquid before it is released. A bulb should be connected between the suction tube and the capillary. L. B.

The Drying of Hides and the Soaking of Dried Hides. H. M. Osborne. *Leather*, 3, 988. Dried hides do not behave uniformly in the soaks. If they have been dried at ordinary temperatures, soaking in water suffices to soften them; but hides dried at a high temperature undergo chemical change, and restoration to the original condition is almost impossible. They may be softened by chemical means, but only at the expense of a considerable loss of hide substance. A method formerly used was to soak the hides in very stale soaks, in which case the softening was done by dissolving out some of the substance by bacterial action. Now the same result is attained with less loss by the use of acid or alkali. Caustic soda solution from 0.1 per cent. to 0.2 per cent. is very efficient, and slightly antiseptic. Carbolic acid. 0.1 per cent. may be added to prevent putrefaction. No time for the duration of soaking can be set. After the bony feel has disappeared, the hides should be washed in a wheel and returned to the soaks. If they firm up on being put back in the soaks, they must be soaked longer. Several repetitions may be necessary. Sodium sulphide may be used with the same precautions instead of caustic soda; the strength of solution may be 0.5 per cent. Acids may be used instead of alkalies, but in this case they must be washed and soaked in clean water before liming, to avoid loss of time and waste of lime. Formic acid is best, strength of solution from 0.1 per cent. to 0.25 per cent. Method the same as with caustic soda. L. B.

The Effect of Scudding on Hides and Skins. *Leather*, 3, 928. Hides and skins are scudded after liming, deliming, puering, bating or drenching. The scudding of hides for sole leather after liming removes any epidermis and hair sheaths which remain, also some short hairs and interfibrillar substance, and also the lime soap made by the action of the lime on the grease of the hide. Some tanners of heavy leather scud after deliming instead of before. because there is less loss of hide substance, the acid used in deliming fixing some of the interfibrillar substance. The disadvantage is that the marks of the scudding tool are more likely to remain. In the case of bated, puered or drenched hides the amount of interfibrillar substance scudded out is greater than in the case of heavy leathers. L. B.

Digitized by Google

Turkey Red Oil, Its Composition and Analysis. F. W. RICHARDSON and W. K. WALTON. *Journal of the Society of Chemical Industry*, 31, 105-8, Feb. 15. The oil examined is extensively used in finishing in the Bradford (England) district. It gives a clear solution in water. It is made from castor oil by the action of strong sulphuric acid. The excess of acid is washed out as far as practicable with a strong solution of salt or sodium sulphate, and the remainder nearly neutralized with ammonia or soda. The authors object to the term "sulphonated" oil as applied to this product, holding that "sulphated" is the correct word. Water was determined by 3 methods. That of Stein, involving stearic acid and saturated salt solution, was unsatisfactory. Ubbelohde's method distils a mixture of 50 cc. oil and 30 cc. of xylol previously saturated with water, and adding a fresh portion of xylol and distilling again. The distillate is collected in a graduated tube. This method gave 50.9 per cent. water. By heating 3.5 gr. in a platinum dish at 100 with frequent stirring until the weight changed in 20 minutes less than 1 mg., the loss was 50.84 per cent. This method the authors regard as satisfactory. For total SO_3, 4 gr. of oil were boiled with dilute HCl ¾ hour, then filtered and thoroughly washed with boiling water. The filtrate gave barium sulphate ppt. equivalent to 3.63 per cent. SO_3. Alkaline sulphates were determined by dissolving in sulphuric ether and shaking out with saturated solution of pure NaCl. The saline solutions were diluted and precipitated with BaCl, giving 0.09 per cent. SO_3. To determine NaCl. shaking out methods failed. A portion was charred, the ash extracted with water and the solution neutralized with N/10 H_2SO_4. The Cl determined by titration with $AgNO_3$ was equivalent to 0.24 per cent. NaCl. Total Na_2O equivalent to 8.41 per cent. Na_2SO_4 was found. Unsaponifiable matter 0.17 per cent. Neutral fat was determined by the Lewkowitsch method, 5.22 per cent. In a second trial using 6 gr. instead of 30 gr., proportions of glycerin and ammonia the same as before, 5.43 per cent. was found. The latter result is preferred by the authors, who afterward omitted the glycerin entirely. The neutral fat gave the following data: Sapon. val., 173.6; Iodine val., 77.73; Yield of glycerol, 13.22 per cent.; Index of refraction at 50° C., 1.467. Fat acids from the neutral fat gave, Sap. val., 188.1; mg. KOH for 1 gr., 298.6; Mean mol. wt., 302.2; Iodine val., 84.42; Refractive index at 50° C., 1.459; Melting point, 4 to 5° C. (Other data are also given.) The neutral bodies contain approximately: unsaponifiable, 3.1 per cent.; di-ricinolein, 13.6 per cent.; tri-ricinolein, 83.3 per cent. When dissolved in 70 per cent. alcohol, the oil gave an acidity equivalent to 32.7 cc. N/1 KOH per 100 gr. of oil. Partial hydrolysis takes place during the extraction. Non-sulphated fatty radicals present as soaps were equivalent to 10.47 per cent. sodium ricinoleate. The total fat, obtained by boiling with dilute HCl and extracting with ether, including some decomposition products due to hydrolysis, is 40.4 per cent. Of this 7.18 per cent. = neutral bodies and 33.22 per cent. = fat acids. The total glycerol found by saponification and decomposition with sulphuric acid was 2.50 per cent.

Digitized by Google

Free glycerol, extracted from the oil by means of a water solution of ammonium sulphate, was 0.82 per cent. In answer to questions Mr. Richardson said he had not found Turkey red oil made from other oils than castor, and that none of those examined contained mineral oils.

L. B.

Formation of Leather by Dehydration. L. MEUNIER and A. SEYEWETZ. *Le Cuir*, 5, 111-15. Knapp treated hide with alcohol, the fibers being thus separated and a pliable substance resembling white leather produced. When wet it quickly returned to the condition of hide. The cost of the process prevented any attempts to utilize it in practice. The well-known dehydrating power of concentrated solutions of mineral salts was recently emphasized by Procter. (See this JOURNAL, VI, 426). The authors had no success with sulphates of feeble bases, *e. g.*, ammonia and zinc. Various mineral salts of high solubility were tried, but either the dehydration was incomplete or the hide was injured. Potassium carbonate, however, has neither of these faults. White hide after draining is hung in a saturated solution of K_2CO_3, containing an excess of the salt in order to maintain the saturation. In the case of thin skins dehydration is complete in 1 to 2 hours, heavy hides requiring 10 or 12. The K_2CO_3 penetrates the hide very little. The solution seems not to wet the surface, behaving as if the hide were oily. After being wiped off the hide dries quickly. A very little of the carbonate shows on the surface of the dried product, which is pliable and strong. Cold water takes some time to reduce it to the condition of white hide, but warm water quickly soaks it. The trace of K_2CO_3 may therefore be removed by rinsing in slightly acidulated cold water. The authors regard this process as an example of formation of leather by purely physical means. They suggest that it may be useful as a means of preserving hides in the white state, at a minimum weight and without salt or other preservative; also that such "leather" stuffed with grease may be serviceable for certain purposes.

L. B.

Reactions of the Tannins. W. EITNER. *Arch. f. Chemie u. Mikroskopie*, 1911. Stiasny's reagent, 10 cc. dilute HCl (1:1), 10 cc. 40 per cent. formaldehyde, boiled 10 minutes with 50 cc. of the tannin solution (invert condenser), precipitates entirely, or nearly so, the catechol tans, comprising those of quebracho, catechu, maletto, mangrove, hemlock, pine (German), aleppo, mimosa, birch, willow, cajotta, oak bark, sumac and gambier. In the filtrate may remain the pyrogallol tans, including those from oak and chestnut woods, knoppern and other galls, valonia and myrobalans; they give a blue or blue violet color with ferric alum (catechol tans give green to greenish black) and may also be tested for with gelatine. Another group reagent is bromine water which precipitates the catechol tans only. A special reagent for the filtrate from the formaldehyde reaction is a 1 per cent. TiK oxalate solution; this gives red

Digitized by Google

precipitates with galls, red orange with chestnut, yellowish red with sumac, myrobalans and oak wood, pale yellow with quebracho, catechu and gambier, and none with mangrove. Yellow ammon. sulphide, containing a moderate amount of polysulphide, serves to distinguish oak and chestnut extracts (abstract, this JOURNAL, 1909 [4], 249). Tin salt, obtained by dissolving 1 part tin in 6 parts HCl, 2 parts HNO_3 and diluting 1 : 25, added drop by drop, precipitates quebracho, canary yellow; mangrove, red, darkening on standing; myrobalans, white; mimosa, pink; catechu, light brown. Tanstuffs can be distinguished by the ratio of tans to non-tans as determined by analysis. Some values are (non-tans = 1): galls 6, sumac 1.8, chestnut 3, oak 2.3, pine bark 1, pine wood 0.75, quebracho 10, mangrove 5, catechu 2. W. J. K.

Report of the Freiberg Experiment Station for 1911. JOHANNES PAESSLER. The number of analyses called for was about the same as in 1910 (report, this JOURNAL, 1911 [6], 200) after allowing for decreases due to guarantees recently furnished to consumers by Hamburg dealers, and the unusual invoice of samples from the colonies in 1910. The tanning materials (73 per cent. of all) were analyzed by both methods, or one, as in 1910. Condensed averages are:

	Tanning substance		Soluble non-tans	
	Shake	Filter	Shake	Filter
Oak bark	10.0	11.1	6.1	5.3
Pine bark	10.5	12.5	9.8	8.4
Mimosa	24.1	33.8	12.3	10.6
Mangrove	38.6	41.0	11.2	8.8
Maletto	40.0	43.5	11.5	8.0
Valonia	28.9	31.9	12.3	10.8
Trillo	39.0	42.8	15.3	12.4
Myrobalans	32.0	35.2	15.7	12.2
seeded	47.0	51.7	21.7	17.3
Divi-divi	43.8	47.5	20.9	17.2
Knoppern	33.8	36.5	8.7	6.0
Quebracho wood	19.7	21.2	2.4	1.5
Chestnut wood	7.9	8.5	1.9	1.4
Sumac	24.9	26.3	16.7	14.7

Investigations made in the institute upon mangrove barks from German East Africa showed these to be valuable from their high tannin content, the age, part of tree taken, time of gathering, etc., all being without influence. Rhizophora and Brugiera gave 28-42 per cent. tannin and Xylocarpus and Ceriops, 27-33 per cent. The first group gives a darker and redder leather, but the color is favored by gathering the bark at the end of the year.

The ratio of non-tans to tans in chestnut wood was about ¼ by the shake method and $^1/_6$ by the filter method, an important matter in extraction.

Digitized by Google

Nothing novel is reported concerning extracts. A report of comparative analyses by both methods is to appear later. W. J. K.

The Use of Zoul's Method for Titration of Fats. HILDEMAR MIELCK. *Chemiker-Zeitung*, 1911 [35], 668. According to Zoul (abstract, this JOURNAL, 1911 [6], 39), the end of the saponification (in glycerin solution) is indicated by quiet boiling; the author could not sharply observe this, for with the necessary heat the liquid always foams. Even with the purest fats 15 minutes at least are needed.

To compare the results obtained by Zoul's method and the usual saponification in alcoholic solution, the fatty acids obtained (about 2 gms.) were vacuum dried 1 hour at 100° and then titrated in alcoholic solution:

	Time of reaction	Acid No.	Freezing-point, °C.
1. Cocoanut oil:			
glycerin	7 min.	204	20.3
"	15 " (nickel dish)	219	20.85
"	15 " (porcelain dish)	222	21.05
"	10 " (oil drop by drop)	260	22.1
"	20 "	271	22.4
alcohol	45 "	271	22.6
2. Colza oil:			
glycerin	20 "	179	16.05
alcohol	45 "	179	16.7
3. Linseed oil:			
glycerin		191	20.5
alcohol		196	22.4
4. Sperm oil:			
glycerin		195	24.45
alcohol		198	23.9
5. Palm-nut oil:			
glycerin		256	23.15
alcohol		257	23.8
6. Bone fat (a):			
glycerin		200	39.9
alcohol		201	39.7
7. Bone fat (b):			
glycerin		196	41.15
alcohol		199	40.15

It is noticeable that the animal fatty acids in Nos. 4 and 7 gave highest freezing points by the glycerin method. Traces of water in glycerin may produce oxy-acids which may explain the differences found with linseed oil, especially in the freezing points. The iodine numbers (Wijs) found with the acids from bone fat were: alcohol, 54.8; glycerin, 49.75, 51.3. The author concludes it is better to use the old method.

W. J. K.

Digitized by Google

The Determination of the Origin of Some Lubricating Oils. N. CHERCHEFFSKY and R. ESCUDIE. *Les matières grasses,* 1911 [4], 2366. The distinction between mineral oils of different sources is the essential theme Chemical methods wholly fail and physical constants only can be relied upon. The following table condenses some of the data:

	Density 15°	Inflamm. degree	Viscosity Barbey	Viscosity Engler	Index refr.	Crit. temp. Dissol.	Crit. temp. Turb.	Riche-Halphen
Russian oil, II	0.899	182	89	14	1:4975	138	39	476
Russian oil, I	0.909	205	53.5	38	5007	144	45	531
Russian oil, oo	0.913	232	25	121	5024	152	55	753
Galician oil	0.917	212	47.5	39	5121	141	33	534
Roumanian oil	0.927	190	47	45	5144	134	23	395
American spindle oil	0.910	221	77.5	22	5100	138	32	480
American cylinder oil	0.891	310	10.5	219	—	194	99	—

The degree of inflammability was determined with the Luchaire apparatus; the viscosity by the ixometer of Barbey, giving the volume of oil flowing in a unit of time at 35°, and by the Engler apparatus showing the minutes required for a unit volume (quoted here for 20° only); for the methods of determining the critical temperatures of dissolution and turbidity and the index of Riche-Halphen, the author refers to earlier articles in the same journal. W. J. K.

The Coefficient of Expansion of Oils Used in the Leather Trade. B. KOHNSTEIN. *Collegium,* 1912, pp. 41-3. The determinations were made with a Westphal balance within the limits 15-65° C., using Dulong and Petit's formula for the computation. Some of the results found were:

Tunny oil	0.000752
Walrus oil (direct fire)	.000714
" " (water boiled)	.000741
Anchovy oil	.000702
Seal oil (fresh)	.00074
Whale oil, brown	.000742
" " light	.000716
Herring oil	.000671
Linseed oil	.000933
" "	.000879
" "	.001002
Shark oil (very old)	.001452
Castor oil	.001084
Neats-foot oil	.000796
Mineral oil (paraffin-free)	.00097

Digitized by Google

Although these constants are not distinctive enough to identify oils, they are considered to be of practical use in computing the volumes of warm oils in vessels, during storage or manufacturing processes. The expansions are high compared with water, which gave the coefficient, 0.000355. W. J. K.

PATENTS.

Process for Clarifying Tanning Liquors. French Patent No. 432,439. A. REDLICH. This process, which applies especially to quebracho, consists in heating the liquor in a closed vessel under atmospheric or higher pressure, then cooling and allowing to settle. The clear liquor is then withdrawn and concentrated.

Bark-removing Machine. U. S. Patent No. 1,017,655. H. L. DRAKE, Medford, Wis.

Machine for Graining and Glazing Leather. British Patent No. 24,710. A. H. STANLEY, London.

Process of Puering Hides and Skins. British Patent No. 24,982. H. BECKER, Frankfurt a. M. The process employs a mixture of bacterial cultures, animal digestive juices, vegetable enzymes, and a substance capable of decomposing fats, such as gall or sulpho-ricinoleic acid.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII MAY, 1912 No. 5

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

CHANGES OF ADDRESS.

P. A. Esten, to 64 North State St., Concord, N. H.
Erwin F. Cords, to 1314 State St., Milwaukee, Wis.

METHODS FOR TESTING LUBRICATING OILS.

By T. D. Simpson.

Research work connected with the Leather industry does not concern itself chiefly with leather oil investigation, but every tannery must have machinery for operation and every portion of movable machinery requires oil or grease for lubrication. Oils vary so much in quality that the best results are only obtained by a selection of the lubricants on an intelligent basis. In the

Digitized by Google

present paper are described some standard methods of determining the most important physical properties of lubricating oils.

GRAVITY.

By this we mean the weight of an oil: *i. e.*, the relation of the weight of a given volume of oil to that of a like volume of water. The two most common modes of stating gravity are in Baumé degrees and directly as Specific Gravity. The former is simpler, and accurate enough for all practical purposes. Commercially, it is universally used for recording the gravity of oils and is determined by means of a Baumé hydrometer, which should be graduated to one-tenth of a degree (0.1°). Such a hydrometer is large, and necessitates the use of a 500 cc. hydrometer jar. When occasion arises to use a small hydrometer, a 100 cc. hydrometer jar is sufficient. The large hydrometer gives more accurate results, and should always be used when the quantity of the oil is sufficient for making the test. The small hydrometer should only be used when the quantity is, say, that contained in a four once ordinary sample bottle. The oil is poured into the jar and the hydrometer floated in it until it comes to rest. Then the reading of the hydrometer is taken at the top edge of the oil. In some cases it is well to put a piece of paper behind the hydrometer jar and use a magnifying glass, as a greater degree of accuracy can be obtained. One tenth of a degree (0.1°) is deducted from the reading to make allowance for the capillary attraction of the oil. Now take the temperature of the oil, and if above or below 60° F. refer to Tagliabue's Manual which reduces the gravity to the temperature of 60° F., which is the standard temperature for the Baumé and specific gravity of oil. For instance, if the gravity of an engine oil is desired, and the reading of the hydrometer was 31.4° Bé. at 78° F., the actual gravity according to the manual would be 30.1° Bé. at 60° F.

The Manual is very convenient, as it saves considerable time in calculation, but where no manual is at hand, the actual Gravity at 60° F. may be calculated by using the factor of 0.0004 as the coefficient of expansion as follows: Assuming the reading and the temperature to be as above, 31.4° Bé. at 78° F.: Proceed by converting the Baumé gravity into the

Digitized by Google

specific gravity by referring to the comparative Baumé and specific gravity table, thus — 31.4° Bé. = 0.8680 specific gravity. The excess in temperature above 60° F. equals 18° F. This is multiplied by the coefficient of expansion 0.0004: 18 × 0.0004 = 0.0072. This added to 0.8680 = 0.8752 giving the actual specific gravity as converted to 60° F. As the Baumé gravity is desired, it will be necessary to again refer to the Baumé and specific gravity table and convert the specific gravity of 0.8752 into Baumé gravity, which gives the result of 30.1° Baumé precisely the same as obtained by using the manual. When the temperature is below 60° F., the result must be subtracted instead of added. Specific gravity can be determined by the specific gravity bottle, the Sprengel Tube or the Westphal's Balance, but for commercial work, it can be accurately enough determined by first taking the Baumé gravity with a large hydrometer and converting into the specific gravity by referring to the conversion tables, or by using the following formulae:

To convert specific gravity into Baumé gravity.

$$\text{Bé.} = \frac{140}{\text{Sp. Gr.}} - 130.$$

To convert Baumé gravity into specific gravity.

$$\text{Sp. Gr.} = \frac{140}{130 + \text{Bé.}}.$$

FLASH AND FIRE TEST.

The flash test of an oil is the temperature to which the oil must be heated to give off vapors, which when mixed with air produces an inflammable or explosive mixture. The fire test of an oil is the temperature at which it will give off vapors, which when ignited will continue to burn. As the personal equation enters into the test to a marked degree, the following points should be considered when the most accurate results are desired.

1. The larger the amount of oil the more vapor will be driven off, hence the lower will be the flash and fire test.

2. From a large and shallow cup the liquid evaporates faster, hence the lower will be the flash and fire test.

3. The faster the oil is heated the lower will be the flash point, as more vapor is driven off.

Digitized by Google

4. The nearer, or what amounts to the same thing, the larger the testing flame the lower will be the flash point. A large flame may produce local superheating.

5. The flame should be applied equidistant between the center and edge of cup, as the mixture of air and vapor is more complete. This is best effected by drawing the flame diametrically across the top of the cup.

6. The thermometers used for taking flash and fire test should be frequently compared with a standard thermometer.

7. Draughts should be carefully avoided.

8. Barometric changes are for practical work negligible. Each five millimeters between seven hundred and forty-five and seven hundred and fifty-five causes a variation of but one tenth degrees centigrade.

There are two kinds of testing, the open and closed, and as the various instruments give different results a description of the method of manipulating the instruments which are most used is hereby given.

OPEN METHOD.

For lubricating oil the Cleveland cup as made by Tagliabue or the Carbondale Machine Company is generally used, and gives the most favorable result. The cup is made of cast steel 21½ inches in diameter and 1¼ inches deep, supported on three legs. It is made in two parts; the lower part is an air bath, in which is set the part for holding the oil. A fairly uniform heating is thus produced, as the flame does not come into direct contact with the part of the cup containing the oil. The cup is freed from the oil accumulated from previous tests by wiping it out with a piece of waste, and then holding it over a gas flame to remove the slightest trace of any oil by burning. When the cup has cooled add the oil to be tested. In the case of neutral, spindle, engine oils, etc., fill the cup to within three-eighths of an inch from the top; cylinder oils to within one-half inch from the top. Now suspend the thermometer by means of a thermometer stand, so that the bulb will be in the center of the oil, and the top of the bulb is just submerged below the surface of the oil. Now apply heat by means of a Bunsen burner or alcohol lamp, adjusting the flame, so that the oil will be heated

Digitized by Google

at the rate of 12 degrees F. per minute. For a test flame a wax taper may be used or a string saturated with oil, or better still a gas flame from a glass tube drawn to a small aperture. The test flame should be about the size of an ordinary match head, and in no case should exceed one-eighth inch in diameter. When the oil starts to vaporize freely the test flame is applied every five degrees, by drawing it diametrically across the top of the cup at a distance of one-quarter inch above the surface of the oil until the flash test is reached, which is indicated by a puffing blue flame. The temperature at this point is the flash test. The fire test is determined by continuing to heat the oil under precisely the same conditions as the flash test, applying the test flame every five degrees, beginning at 30 degrees above the flash test for neutral oil and 45 degrees above for cylinder oils until the oil continues to burn. The temperature at this point is the fire test. The burning oil can be extinguished by means of a cover that comes with the cup, but it is advisable to extinguish it by simply blowing it out thereby allowing the thermometer to remain in the oil and cool gradually, rapid cooling being injurious to thermometers. In testing 300 oil, the oil should be heated at the rate of 5 degrees per minute.

Open Method for Illuminating Oils. The instrument generally employed for taking the flash and fire test of burning oils is the open fire tester as made by Charles J. Tagliabue, and the official method for taking a test on this cup is as follows: The instrument should stand level. Fill the metal bath cup with water of about 60° F., leaving room for displacement by the glass oil cup, which is then placed in the bath. Fill the glass oil cup with the oil to be tested to within one-eighth inch of its upper level edge. See that there is no oil on the outside of the cup, or upon its upper level edge, using soft paper to clean the cup in preference to cotton or woolen material. Adjust the horizontal flashing-taper guide-wire in place. Suspend the thermometer, with the bulb of same well covered by the oil. Heat bath with small flame lamp, alcohol, gas or other, having the flame so adjusted that it will raise the temperature of the oil not faster than 2 degrees F. per minute, without removing the lamp during the whole operation. Remove air bubbles, if any, from the surface of the

Digitized by Google

oil before first trial for flash is made. At the proper trial temperatures, try for flash with a small (not over one-eighth inch) bead of flame on the end of a piece of lighted twine (stiffened by wetting and twisting) or a broom splint, by drawing it quickly and without pause across the guide wire from left to right. The first or initial flash obtained is called the flashing point. Successive flashes are looked for, until the oil surface ignites and continues to burn until quickly blown out. This burning point temperature is called the fire-test.

VISCOSITY

Commonly called the body of an oil; scientifically it is the opposite of fluidity, and is due to internal friction. In most cases the viscosity of an oil determines to a considerable extent its value as a lubricant. By making a comparative viscosity test with an oil of known value that has given satisfactory results in practice, the lubricating value of an oil for a given purpose may be pretty definitely determined. A description of the official method for taking tests with one of the recognized instruments used in the United States is as follows:

SAYBOLT'S UNIVERSAL VISCOSIMETER.

This instrument is arranged specially for testing cylinder, valve and similar oils, with bath at 212° F., and oils at 210° F. It may be used with either gas or steam alone, or both in combination. If both, are used, the steam may be introduced slowly to replace evaporation depending chiefly upon the gas flame to raise the temperature to the boiling point, and keeping it there during the test. The bath vessel should always be kept full during a test.

Directions for making the test at 212° F.

1. Have the bath of water prepared at the prescribed temperature.

2. Have the oil strained into one of the tin cups, in which cup it may be heated up to about the standard temperature.

3. Clean out the tube with some of the oil to be tested by using the plunger sent with the instrument. (No drill or other instrument should be used.)

4. Place the cork (as little distance as possible) into the lower outlet coupling tube just enough to make air tight, but not

Digitized by Google

far enough to nearly touch the small outlet jet of the tube proper, (⅛" to ¼" may be enough).

5. Pour the oil from the tin cup (again through the strainer) into the tube proper until it overflows into the overflow cup up to and above the upper edge of tube proper.

6. Now again see that the bath is at the prescribed temperature.

7. Use the thermometer sent with the instrument, stirring the oil until it comes just to the standard temperature.

8. Remove the thermometer.

9. Draw from the overflow cup with a pipette, all the surplus oil down to, and below the upper edge of tube proper; this insures a positive starting head.

10. Place the 60 cc. flask under and directly in line with the outlet jet, and as close to the coupling tube as is practical to permit of room for drawing the cork.

11. With the watch in left hand draw the cork with the right, and simultaneously start the watch.

12. The time required in the delivery of 60 cc. is the viscosity.

In testing reduced black oils, bath and oil are heated to 130° F. In testing spindle, paraffine, red and other distilled oils, bath and oil are heated to 100° F. When used at 130° or 100°, gas alone is used to bring the bath to the prescribed temperature, and turned off during the test, the large size of the bath usually permitting one test to be made without re-heating. Directions for making the test at 100° and 130° F. are exactly the same as those given for the higher temperature.

THE PIPETTE VISCOSIMETER.

This is a form of viscosimeter used by the Pennsylvania Railroad. The Pipette Viscosimeter consists of an ordinary 100 cc. long bulb pipette. It is graduated so as to hold 100 cc. to the bottom of the bulb, and the apperture of the pipette is so made that 100 cc. of water at 100° F. will run out of the pipette in 34 seconds. The bulb of the pipette varies from 1⅜" to 1½" outside diameter. The oil is heated to the required temperature, care being taken that it is uniformly heated, and is then brought up into the pipette to the required mark. The time taken for

Digitized by Google

the oil to run out of the pipette to the bottom of the bulb gives the test figure. This method is not so accurate as using an ordinary viscosimeter, but gives a fair approximation to the viscosity of an oil by comparing with an oil of known viscosity. Furthermore, a pipette for determining comparative viscosities may be used when the sample is not of sufficient quantity to have the viscosity taken on any of the standard instruments. By testing the oil, whose viscosity is sought with a 50 cc. pipette, and then testing an oil of known viscosity in the same manner, an idea can be obtained of the comparative viscosity of the two oils.

COLD TEST

Is the temperature where the oil congeals or ceases to flow. To take the cold test fill an ordinary 4 ounce sample bottle one-third full with the oil whose cold test is desired. Insert a cork or rubber stopper perforated to receive the thermometer stem. The thermometer is then inserted, taking care that the bulb is in the center of the oil. Now place the bottle in a suitable receptacle; surround it with a freezing mixture of ice and salt. Allow the oil to remain thus until the thermometer reading indicates that the temperature is approaching the congealing point. Then remove and note if the oil is congealed. If not, replace it quickly and allow it to remain until the temperature has dropped 2 degrees, then again remove to observe the condition of the sample. This is repeatedly done every two degrees until being removed from the freezing mixture it is congealed. The temperature at this point is recorded as the cold test.

As a rule in the refinery the sample can be chilled in the brime solution such as is used in connection with the refrigeration process for chilling wax. To make cooling mixtures to be used at a temperature above 35° F. used cracked ice and water, between 35° and 0° F., use 2 parts of ice and 1 part salt and from 0° to — 30° F. use 3 parts of dry calcium chloride and 2 parts of ice or snow. Carbolic acid dissolved in ether readily gives — 50° F.

Cloud Test. The Cloud Test of an oil is the temperature at which it begins to get turbid. It is taken in a similar manner to the Cold Test, excepting that the temperature is noted when

Digitized by Google

a well defined flocculent cloud appears around the thermometer bulb. The cloud test is taken by filling an ordinary four ounce sample bottle with the oil whose clould test is desired, and inserting a regular cold test thermometer so that the bulb will be in the center of the oil. Now proceed as in taking the cold test, by placing the oil in a suitable receptacle and surrounding it with a freezing mixture of cracked ice and salt. After cooling down to say within 10 degrees of the cloud test remove the bottle every 2 degrees and note the appearance.

THE PURIFICATION OF TANNERY EFFLUENTS.[1]

Some interesting experiments have been carried out by Messrs. Hein, Faure-Fremiet, Herbert, Moussee, Sarbory and Schöffer, on the purification of tannery effluents. The experiments were made with a soak water containing a large amount of organic matter and a sodium sulphide solution used for unhairing. The results obtained by various methods of purification are given below.

PURIFICATION BY MECHANICAL MEANS.

The effluent of the water used for soaking was allowed to stand for five to six hours, the greater part of the solid matter of a granular and gelatinous nature was thus deposited, colloidal substances being left in the liquid. The amount of deposit thus obtained amounted to not more than 250 grammes in the dry state per 1,000 liters of the liquor. It was found that although little purification was brought about by mere settling, the liquor could be rapidly clarified by thoroughly mixing the liquor with water containing clay in suspension.

Similar results were obtained with the unhairing solution containing sodium sulphide, the amount of deposit obtained by settling in this case being about 1,250 grams in the dry state per 1,000 liters. The process of Messrs. Michoëlis and Rona for precipitation of albuminoids in alkaline solution was also utilized. For practical use a mixture of colophany, denatured methyl alcohol and water is recommended instead of the mastic and ethyl alcohol emulsion, which is too expensive. Investigations have been made, and are almost complete, on the conditions

[1] *Leather World*, 4, 119-20 and 144-5.

Digitized by Google

under which colloidal sulphur is precipitated by this method and the industrial use of the sulphur so obtained.

PHYSICO-CHEMICAL CLARIFICATION.

In this method substances were used which produce coagulation, and thus bring about a more rapid deposition of impurities. Among the various materials which can be used for this purpose, lime, ferric sulphate and aluminum sulphate were tested. In alkaline solution, aluminum sulphate gives the most voluminous and gelatinous precipitate, and is therefore expected to bring about a better and quicker deposition. When using ferric sulphate and aluminum sulphate, precipitation was therefore accelerated by making the water slightly alkaline with lime.

The quantity of reagents necessary to produce clarification of soak water is about 0.5 to 1 kilogram per 1,000 liters of soak liquor.

When lime alone was used the water was colorless and odorless; with sulphate of iron and aluminum, the odor was greatly decreased and the purified liquid perfectly limpid and fluid. When lime was employed as the clarifying agent, the purified effluent was slightly alkaline, and in the other cases it was slightly acid.

With lime and aluminum sulphate, the organic matter in the soak liquor was reduced to about half the amount originally present. The total nitrogen was reduced from 0.092 gram to from 0.033 to 0.070 gram per liter; ammoniacal nitrogen was reduced from 0.012 gram to from 0.005 to 0.008 gram per liter; sulphuretted hydrogen was completely removed, and fatty matters present were also decreased. From the chemical point of view, therefore, the purification is relatively satisfactory, especially with lime and aluminum sulphate. Ferric sulphate was not found so efficient as aluminium sulphate. The quantity used was ½ kilogram per 1,000 liters.

With regard to physical properties, it was found that when ferric sulphate was employed the electrical conductivity of the effluent diminished from 28.88×10^4 to 19.45×10^4; with aluminum sulphate the conductivity was found to increase to 51.98×10^4, due to the slight acidity acquired by the liquid. When lime was employed as the clarifying agent the conductivity

Digitized by Google

increased to 78.52×10^4 on account of the small percentage of lime dissolved in the water.

The number of germs per cubic centimeter of the water was reduced from 2,000,000 originally present in the soak liquor to 4,000 in the purified effluent when ferric sulphate was used. When lime was employed, the number of germs per cc. was diminished to 71,000, and with aluminum sulphate as the purifying agent, the number of germs in the purified effluent was 81,000.

The deposit obtained from the soak liquor by the above methods of clarification was weighed, dried and analyzed in order to determine its value as a fertilizing agent for agricultural purposes. The following results were obtained per 1,000 liters of soak liquor effluent:

	Lime grams	Aluminium sulphate grams	Ferric sulphate grams
Dry deposit obtained	150.0	150.0	626.0
Nitrogen	1.41	0.63	3.15
Phosphoric acid	0.54	0.15	13.29
Lime	421.80	0.30	2.45
Potash	3.15	1.33	4.38

These results show that where sufficient space is available to drain off and dry the slime deposited from the effluent, some profit might be derived from its use as a fertilizing agent.

With the sodium sulphide solution used for unhairing, similar results were obtained by use of the above compounds for clarifying the effluent, lime, however, being an exception. When lime was used, the clarified liquor was yellowish in appearance, almost odorless and very alkaline. The total nitrogen was decreased from 1.960 grams to 0.908 grams per liter; the ammoniacal nitrogen from 0.081 to 0.013 grams per liter; fatty matters were decreased. The effluent was thus greatly improved, but the clarified liquor always contained large amounts of sulphuretted hydrogen, the amount remaining practically constant.

When lime was employed, the number of bacteria was reduced from 500,000 to 81,000 per cc., and the deposit on analysis gave the following results per 1,000 liters of the effluent:

Digitized by Google

	Grams
Dry deposit	22,500.0
Nitrogen	31.5
Phosphoric acid	2.25
Lime	8,721.0
Potash	128.25

From the amount of fertilizing elements thus present this deposit should be worth collecting and drying for use on the soil.

PURIFICATION BY CHEMICAL REACTIONS.

This method differs from those given above in that substances were used which react chemically on the impurities present in the water. The reagents tested for this purpose were: (1) A mixture of ferric sulphate and chloride of lime; (2) calcium permanganate; (3) sodium hypochlorite.

These reagents were added to the effluent until no further precipitation took place and until the odor of the soak water was removed. The quantity of reagents employed per 1,000 liters of effluent was as follows:

	Grams
Ferric sulphate	250
Chloride of lime	200
Permanganate of lime	100
Sodium hypocalorite	3,000

The soak liquor, after treatment with the above reagents, was allowed to stand for a few hours to allow the precipitate to deposit. The clear solution thus obtained was slightly yellow in color, the putrefactive smell was greatly diminished. When reagents (1) and (3) were used, the smell of the purified liquor resembled that of chlorine.

The purified effluent was slightly acid when ferric sulphate and chloride of lime were employed, neutral when calcium permanganate was used, and slightly alkaline when the precipitating reagent was sodium hypochlorite.

With reagents (1) and (2) the organic matter present was decreased, but this was not estimated when sodium hypochlorite was employed. Total nitrogen was reduced from 0.075 gram per liter to 0.056 and 0.067 gram per liter respectively when the first two reagents were employed. With sodium hypochlorite the total nitrogen was reduced from 0.092 gram to 0.078 gram

Digitized by Google

per liter. The amount of ammonia was diminished considerably with the two first reagents, and practically completely removed with sodium hypochlorite. Sulphuretted hydrogen was reduced and fatty matters were decreased.

Ferric sulphate and chloride of lime reduced the number of germs originally present in the soak water to 640 per cc. With calcium permanganate, purification in this respect was greater and sterilization was complete.

Sodium hypochlorite charges the water with chlorinated compounds, renders it alkaline, and reduces the number of germs to 8,500 per cc.

Though purification is satisfactory when the above chemical reactions are employed, the result was found to be inferior to that obtained with the clarifying agents previously mentioned, especially with lime.

The following analysis of the deposit obtained when the three chemical reagents given were used shows that it possesses little fertilizing value:

	Ferric sulphate and chloride of lime grams	Calcium permanganate grams	Sodium hypochlorite grams
Dry deposit obtained.....	85.00	123.00	400.00
Nitrogen	0.23	0.27	3.25
Phosphoric acid	2.78	0.39	0.26
Lime.....	3.07	6.88	0.52
Potash	2.04	1.47	0.88

The quantities given are per 1,000 liters of liquor.

With the sodium sulphide effluent used for unhairing, the following reagents were used: Ferric sulphate, alumina sulphate, mixtures of 5 parts ferric sulphate and 2 parts chloride of lime, calcium permanganate and sodium hypochlorite.

These reagents were all found to considerably improve the appearance of the effluent, especially ferric sulphate, alumina sulphate, and calcium permanganate, but the purified effluent still contained a considerable amount of sulphuretted hydrogen. The best results seemed to be given with ferric sulphate, which is also cheaper.

With these reagents the viscosity of the effluent was greatly decreased, especially when ferric sulphate was employed. The calcium permanganate and mixture of ferric sulphate and chloride

Digitized by Google

of lime reduced the surface tension of the effluent to the greatest extent, though in all cases it was decreased. The variation of these physical constants is worthy of note, considering the great alkalinity of the purified effluent.

The use of ferric sulphate decreases the number of germs to 5,000 per cc.; with ferric sulphate and chloride of lime in admixture the number of germs were reduced to 1,500 per cc.; sodium hypochlorite diminished them to 7,200; and aluminum sulphate to 49,000; while calcium permanganate completely sterilizes the water.

On analysis of the deposits the following results were obtained, quantities referring to 1,000 liters of effluent:

	Ferric sulphate kilograms	Aluminum sulphate kilograms	Ferric sulphate and chloride of lime kilograms	Calcium permanganate kilograms	Sodium hypochlorite kilograms
Dry deposit obtained ...	10.50	33.05	3.87	4.04	3.50
	Grams	Grams	Grams	Grams	Grams
Nitrogen.....	38.43	78.40	8.67	7 92	43.40
Phosphoric acid.....	11.65	1.92	7.66	11.31	0.87
Lime	282.20	78.40	582.32	743.36	5.25
Potash.....	30.45	188.65	69.93	64 46	104.30

These deposits should be of value as fertilizing agents.

From the experiments thus carried out, Mr. Heim concludes that though the water is considerably improved, except as regards amount of sulphuretted hydrogen present, the cost of the process for this result is too great unless the deposit could be satisfactorily utilized. In order to compensate further for the expense of purification, experiments have been, and are still being, carried out in order to recover the sulphur from the effluent. This would be very valuable as a by-product.

Two methods for this purpose have been tested by Mr. Heim. Using the method with mastic, already referred to, a light yellow water was obtained possessing a smell of resin, quite fluid and slightly acid. The total nitrogen was reduced from 1.960 grams to 0.728 gram; ammoniacal nitrogen from 0.081 gram to 0.068 gram; and sulphuretted hydrogen from 10.241 grams to 1.423 grams per liter.

The second process investigated consisted in agitating the effluent with clay, afterwards acidifying with sulphuric acid, then filtering or decanting off the clear solution.

Digitized by Google

A light yellow acid solution, smelling slightly of sulphuretted hydrogen, was thus obtained. The total nitrogen was decreased from 1.96 to 0.56 gram; ammoniacal nitrogen from 0.81 to 0.065 gram; and sulphuretted hydrogen from 10.241 grams to 0.758 gram per liter. The number of germs was greatly reduced. A considerable amount of sulphuretted hydrogen was liberated during the process, the sulphur from which could be recovered by processes similar to those employed for purifying coal gas. The effluent also, after purification, grows more and more turbid, due to the deposition of colloidal sulphur. This can be coagulated with lime and then collected. Experiments are being made on the sulphur thus recovered with a view to employing it for making mixtures for use in agriculture.

BIOLOGICAL PURIFICATION.

From experiments made in the purification of soak liquor, Mr. Heim concluded that, leaving out of account the relative cost of the different processes, it was impossible to obtain sufficient purification by the aid of ærobic or anærobic organisms without extending the work to an extent which would not be practical in this industry. Purification by direct filtration on bacteria contact beds, and also by filtration after fermentation, is very satisfactory from a bacteriological point of view, but is much less satisfactory with regard to chemical composition. If the septic tank is first employed, a considerable decrease in organic matter is then obtained on the bacteria beds. This is not the case if the effluent is conveyed directly into the bacteria beds. In both cases, however, the total ammoniacal nitrogen is not decreased to any considerable degree. Taking into account the chemical composition of the effluent before and after, as well as the number of germs present, the results obtained by biological methods of purification were inferior to those obtained by chemical purification.

ACIDS IN TAN LIQUORS.[1]

By Professor H. R. Procter.

The very interesting paper on this subject read by Messrs.

[1] *Shoe and Leather Reporter*, March 21, 1912.

Digitized by Google

Kerr and Wilson at the last convention of the American Leather Chemists' Association leads me to think that a few words from myself may not be without interest to your readers. The uses of acid in the liquors are various. Where lime is used as an unhairing agent, acids are often necessary to remove its last traces, and for this any acid will do which gives soluble lime-salts. In sole leather tanning, acid plumping in the liquors is also desired, and for this purpose relatively strong acidity is needed.

Beside these two requirements, a certain amount of acidity appears to be necessary to enable the vegetable tanning process to go on at all, though of its amount and the mode of its action our knowledge is at present very imperfect. Certain it is that alkaline liquors will not tan, though they may color; and that tannin and gelatine absolutely free from acids and their salts will not mutually precipitate. Gelatine and hide fiber belong to the peculiar class of bodies known to chemists as "amphoteric," which are neither distinctly acid nor basic, but capable of acting in either sense. In presence even of weak acids, they form compounds which apparently are of the nature of salts, which are capable of precipitation with tannins, while the pure gelatine is not. Weak, however, as gelatine and hide fiber are as bases, they seem capable in some cases of decomposing salts and appropriating their acid, and perhaps also their basic constituent; and therefore we may regard the study of the salts always present in extracts and liquors as not less important than that of the acids themselves, though even less completely understood.

One action of the salts, however, has of late received some attention, but its practical importance is still scarcely appreciated by the tanners—that is the effect of the salts of chemically weak acids in rendering those acids still weaker, without diminishing their power of combining with bases, as for instance, of neutralizing and dissolving lime, or of changing the color of such indicators as are sensitive to the weakest acids, such as phenolphthalein. This may be clearly shown by the following simple experiment. A measured portion of dilute acetic acid is placed in a glass with a few drops of phenolphthalein and of some indicator less sensitive to acids, such as congo-red, methyl-orange, or even litmus, and standard caustic soda is added from a burette.

Digitized by Google

At a certain point (before the whole of the acid is neutralized) the congo-red will change color, but appreciably more soda must be added before the phenolphthalein becomes pink, showing the true neutrality. If now a further equal portion of acetic acid be added to the used liquor, and the test repeated, the phenolphthalein will give practically the same test as before, but the congo-red will show a still lower result, owing to the weakening of the acid by the neutral sodium acetate formed in the first operation.

It must not be concluded from this that congo-red is a bad, or phenolphthalein a good indicator; for if a similar experiment be made with the weak alkali ammonia, it will be the congo-red and not the phenolphthalein which will show the true reading, the former being sensitive to the very weak acids, and the latter to weak alkalies. Practical use is constantly made in Europe of this effect of neutral salts in deliming;—acetic, lactic or butyric acid is added to the liquor left by a previous operation, and its swelling power is partially or wholly paralyzed by its neutral salt in the liquor, while the solution of lime is unaffected. In this way all the effects of bran drenching are obtained, and the exact degree of plumping required can be regulated by each time running away and replacing by water a suitable portion of the liquor.

Appling these facts to our consideration of the tannery liquors, we can see that the mere determination of total acidity, with any single indicator, such as hematin or phenolphthalein gives no useful information; a fact which has been very fully insisted on by Messrs. Kerr and Wilson. A more practical method is to take advantage of the sensitiveness of different indicators to different degrees of real acidity. Congo-red changes color very approximately at the lowest acid strength which will perceptibly plump hides, and may be adopted as the indicator for acids available for plumping. The old lime-water method is fairly exact in good hands, and gives a direct report as to lime-dissolving acids; while for total acid, hematin or phenolphthalein are suitable, and for several reasons the former is preferable, though it has a gradual color change through several tints, and practice is needed to get uniform results. Phenolphthalein is sharper, but does not indicate real neutrality but a very slight degree of

Digitized by Google

alkalinity, which tends to oxidation and darkening of the test liquor.

I prefer the method of spotting on test-paper with a glass rod to previous precipitation of tannin with gelatine, which is necessary if the indicator is to be used in the liquor, and is both troublesome and liable to remove acid. The acidity of pure tannins is so small that it is quite negligible, especially if hematin is used. Congo-red paper can be bought or made. Hematin paper is easily prepared by dipping blotting paper in the solution, and can be kept dry in the yellow state, but is best used wet on a white tile, and if required blue, must be made so with a drop or two of ammonia in a beaker of water just before use, and well washed.

In all spotting titrations it is best first to test rapidly, adding 1 cc. of the standard solution at a time, and then do a second test, adding at once to the nearest cc. and completing drop by drop. Oxidation can be wholly prevented by titrating in a flask with addition of a drop or two of gasoline (ware lights!); but is only serious if phenolphthalein is used. If knowledge is desired of other degrees of acidity, other indicators can be chosen, of which there is a large range.

As to the use of the results when got, I can only suggest for the present that they should be noted when tanning is satisfactory, and any change from these standards should be a warning signal for special care and close observation. At the same time I would echo and emphasize Messrs. Kerr and Wilson's protest against the waste of time in unimportant routine work, and the neglect of technical research which obtains in many tanneries both American and English. In a systematically worked tannery the routine should run of itself and only require a small amount of testing to ascertain that the machine is working rightly; but the possibilities in front of chemical research are absolutely unlimited and revolutionary. As an English tanner put it to me the other day, the trade is "walking on the edge of a precipice," with no notion of the surprises which chemistry has in store for it. When the trade realizes this, the real chemists will come by their own, and the mere "analyzing machine" will take a back seat!

Digitized by Google

A METHOD FOR THE QUANTITATIVE DETERMINATION OF THE FALLING OF SKIN IN THE PUERING OR BATING PROCESS.[1]

By Henry J. S. Sand, Joseph T. Wood and Douglas J. Law.

As is very generally known, the skin, in the course of leather manufacture, is before tanning subjected to the liming and then

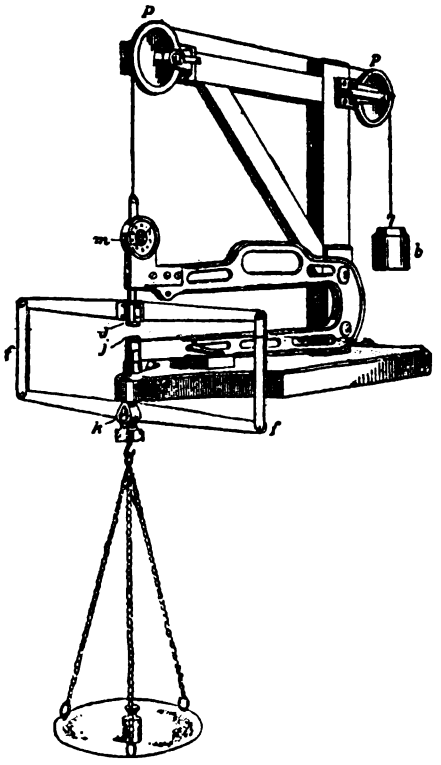


Fig. 1.—Apparattus for measuring degree of falling.
m = micrometer dial. JJ = jaws between which the skin is placed. *b* = balance-weight attached to cord passing over pulleys *pp*, to counterbalance weight of frame, pan, etc. *k* = knife edge supporting pan and weights *w*.

to the puering or bating process. In the former, it is "plumped," *i. e.*, it takes up a large amount of water which causes it to swell and to acquire a considerable degree of resiliency. In the latter process in which it is treated with an infusion of dog or other

[1] *J. Soc. Chem. Ind.*, 31, 210-13, March 15, 1902.

Digitized by Google

manure, or with artificial bates the skin falls, *i. e.*, the water appears to leave the interior of the cells, an appreciable quantity of the material of which the latter are composed goes into solution, and the skin should become soft and practically lose its resiliency completely. For the purposes of leather manufacture an experienced operative can tell in a perfectly satisfactory manner, whether a skin has been properly puered or not, by experience. For scientific investigations, however, on the relative efficiency of different bates, it becomes desirable to possess a method which will allow us to express the degree of falling in a quantitative and objective manner. In the following process this is done by measuring the resiliency of the skin. A piece of the latter is subjected to successive increasing and then decreasing pressures and its thickness is measured under each load.

Fig. 1 shows the apparatus* that we have employed for this purpose. It consists essentially of a commercial form of micrometer sold for the purpose of measuring the thickness of leather. A pan for weights is attached to one of its jaws by means of the frame *f. f.*, in such a manner as to secure a perfectly straight pull. The weights of the frame and pan are counter-balanced in the manner shown, by the counterpoise *b*.

This apparatus proved perfectly satisfactory for heavy loads. For light loads, however, the results are somewhat vitiated by the very considerable friction shown by the rack and pinion of the micrometer. The difficulty was got over to a certain extent by inserting rollers into the micrometer and supplying it with large jaws up to a cross-section of ten square centimeters. A correction was also made by placing a weight approximately equal to the friction in the pan while loading; and on the counter-poise while unloading.

Fig. 2 represents an apparatus* which has been designed so as to be free from the faults inherent in the form just described.

It consists essentially of a balanced lever, A, to which the

* The apparatus was constructed by Mr. W. Linney, of the University College, Nottingham.

Since this apparatus was constructed Professor H. R. Procter has informed us that an appliance devised by Mr. Anderson, of the Leeds University, for measuring the thickness of leather under varying pressures, has been in use in the Leather Industries Department for some months for the purpose of measuring the proportion of the permanent to the elastic compression.

Digitized by Google

upper jaw, J, is rigidly attached. By means of a sliding weight, W, various loads from zero upwards may be put on this jaw.

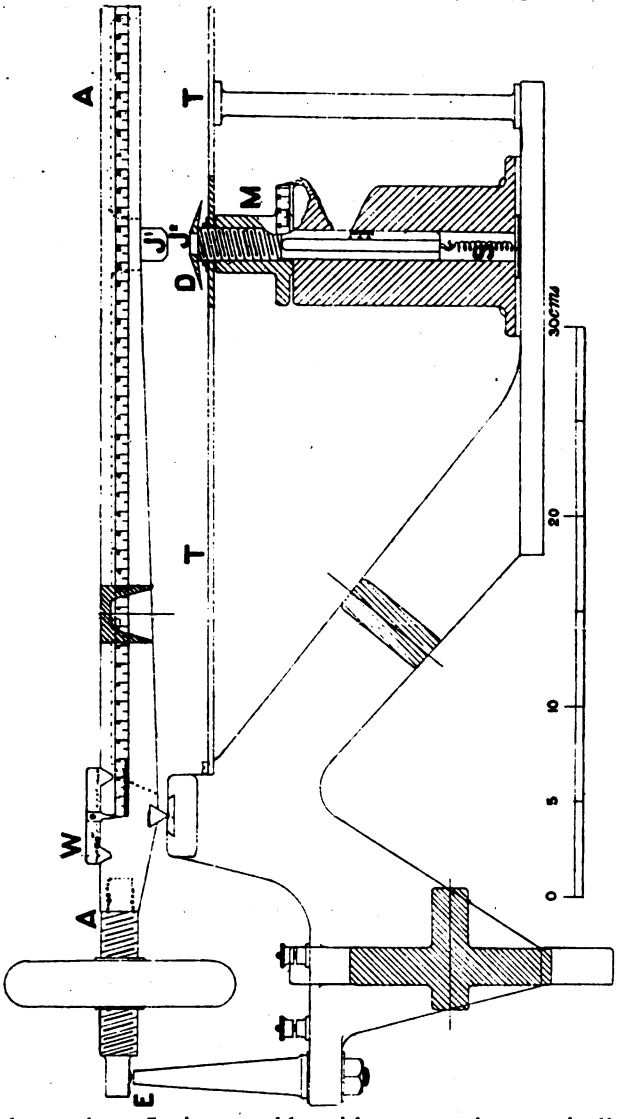


Fig. 2.

The lower jaw, J_2, is movable without rotation vertically up and down, its position being controlled by the micrometer-nut, M, in conjunction with the spring, S. To use the apparatus the piece

Digitized by Google

of skin is laid on the table, T the weight, W, is placed in the desired position and the micrometer-nut, M, adjusted until the lever, A, is brought to what we shall call its normal position, which is detected by means of the contact device, E, of Shaw's electric micrometer. As is known this consists of an electric circuit made up of a dry cell, a telephone and the contact device proper comprising a small iridio-platinum contact plane and a slightly larger iridium plate. The making or breaking of contact which shows the correct position of the lever during loading or unloading respectively is indicated with very great accuracy by the telephone, and the thickness of the skin may be accurately read by the position of the micrometer-nut, M, conveniently illuminated by a small electric flash-light. The tapered disc, D, causes the water forced out of the skin to run on the table, T, and thus keeps it away from the screw of the micrometer.

Load per sq. cm. in grm.	Thickness in mm.		
	Limed skin	Puered skin	Δ
0	3.45	1.78	1.67
20	3.43	1.58	1.85
40	3.33	1.43	1.90
60	3.28	1.35	1.93
80	3.22	1.23	1.99
100	3.15	1.13	2.02
120	3.08	1.08	2.00
140	3.03	1.05	1.98
160	2.95	1.01	1.94
180	2.90	0.98	1.92
200	2.83	0.95	1.88
300	2.73	0.88	1.85
All off	2.98	—	—
380	2.61	0.82	1.79
600	2.43	0.76	1.67
All off	—	0.76	—

Δ = difference in thickness of the skin in the limed and puered respectively, *i. e.*, compression under the same load.

The table gives representative numbers obtained on the same sheep-skin (roan) in the limed and in the puered condition. The results are expressed graphically in Fig. 3.

The following is a brief summary of the results obtained thus far: A limed skin is first compressed, and then on releasing the pressure recovers more or less of it s former thickness, according to the amount of plumping it has received, *i. e.*, it shows a

Digitized by Google

certain amount of resiliency. A well puered sheep-skin, on the other hand, shows no resiliency at all, *i. e.*, on releasing the pressure the whole of the compression persists. In the case of an ox-hide subjected to a bate of hen-dung, a slight recovery takes place on releasing the pressure. This accords with the fact that it will never be possible to puer a thick ox-hide so effectively as a thin sheep-skin. A piece of india-rubber, on the other hand, is completely resilient, *i. e.*, it wholly recovers its thickness on releasing the pressure. The relative thickness of the same skin in the limed and puered conditions under varying loads is also of interest. The process of puering may, as a rule, be taken to reduce a limed skin to between two-thirds and one-

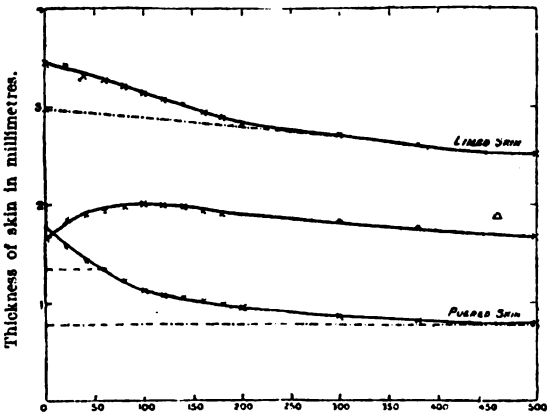


Fig. 3.

Load in grams per square centimeter.
The dotted lines show the thickness on taking off the load.

half of its thickness in the swollen condition. If both limed and puered skin be subjected to the same load, the puered skin will at first be compressed very much more than the limed one. This is probably due to the expulsion from it of water, held simply by capillary attraction. On further increasing the load, however, the compression decreases greatly in the case of the puered skin; with both limed and puered skin increase of compression ultimately becomes practically proportional to increase of pressure, and is slightly greater with the former than with the latter.

Digitized by Google

DISCUSSION.

MR. DUNFORD inquired whether it was necessary to carry out measurements on the same parts of a skin before and after puering, or whether the authors took the mean of a large number of measurements from different parts of the skin.

MR. HARVEY asked whether measurements made on different parts of the same piece of skin varied much and what was the amount of divergence.

MR. WOOD, in reply, said that as a rule only small pieces of skin had been taken, so that the pieces measured before and after puering were not far apart. The compression curves obtained from different parts of the same skin were not identical but showed the same general form. If it was desired to obtain an average compression curve for a skin the simplest plan was to double it up before putting into the apparatus and to divide the measured thickness by two.

NOTES ON THE ESTIMATION OF GLUCOSE IN LEATHER.[1]

By Dr. J. Gordon Parker and J. R. Blockley, M. Sc.

The estimation of glucose in leather is usually a *bête noir* to the leather trades chemist, for it involves so many operations; and, although it is possible to obtain fairly close duplicates in one solution, the results of a second complete analysis do not always agree very well with the first.

Various simplifications of the original Von Schroeder method have been advanced from time to time, and in the coöperative work on leather analysis for the American Leather Chemists' Association for 1911, part of the work consisted in comparing the effect of normal and basic lead acetates for the detannization of the water soluble matter solution. In the experiments of one of us, it was found in every case that, when normal lead acetate was used for the detannization, a higher result for the percentage of glucose was obtained than when basic lead acetate was used. The following experiments were undertaken to discover if possible, what the cause of this divergence was, and also which of the two results, that obtained by using normal lead

[1] *J. Soc. Chem. Ind.*, 31, 268-9, March 30, 1912.

Digitized by Google

acetate and that by using basic lead acetate, was the more correct one.

In a large number of experiments the average percentage of glucose found in a sample of weighted leather was 8.7 when normal lead acetate was used, and 7.8 when basic lead acetate was used for the detannization of the water soluble matter solution. The same sort of result was obtained with other leathers containing glucose, the percentage always being higher when the normal acetate was used. It was thought that the discrepancy between these two results might arise in the following way: The water soluble matter solution from a leather containing glucose would consist of uncombined tannins, glucose, a certain amount of free organic acids such as acetic, and non-tannin matters like gallic acid.

A typical analysis of such a soultion is:

	Per cent.
Tanning matters	11.1
Glucose	7.2
Other non-tanning matter	3.7
Total soluble matter	22 0

Some of these other non-tanning matters, such as gallic acid, reduce Fehling's solution, and hence would be reckoned as glucose if they were not removed in the detannization process. (Procter states* that gallic acid does not reduce Fehling's solution, but we find that it does.) Since gallic acid will reduce Fehling's solution, it is essential that, for accurate work, it should be removed before the actual reduction operation takes place. Gallic acid is precipitated by normal and by basic lead acetate, so that in the ordinary process of detannization the gallic acid should be removed. Gallic acid is, however, not completely precipitated by lead acetate in acid solution. If acetic acid be added to a solution of gallic acid, and lead acetate added, then no precipitation takes place, and it was thought that herein lay the cause of the afore-mentioned discrepancy.

If the water soluble matter solution contains some organic acid, such as acetic or lactic, as it almost undoubtedly would in the case of a vegetable tanned leather, then the addition of lead acetate would not remove the whole of the gallic acid, the amount

* Leather Industries Laboratory Book, p. 121.

Digitized by Google

left in solution depending on the amount of acetic or other acid present. It is here that the difference between normal and basic lead acetates arises.

The amount of free acetic acid would be less when the basic salt is added than when the normal salt is added, because, in the former case, some of the acid would be neutralized in forming the normal acetate from the basic. Hence, with the use of basic lead acetate there is less free acid, a more complete removal of gallic acid and a lower result for the percentage of glucose. Both basic and normal lead acetates are liable to the same sort of error, but to a less extent in the case of basic than normal.

Experiments were performed on standard solutions of chemically pure glucose. The first series was made on a solution containing 0.5 per cent. of glucose and 1 per cent. of gallotannic acid. This solution was treated in the same way as a water soluble matter solution would be treated. It was detannized, in one case with normal lead acetate, and in another with basic lead acetate, and the succeeding operations were as usual. The percentage of glucose found was the same in both cases, 0.51 per cent. (actually present, 0.50 per cent.). From this it was concluded that the method of analysis was sufficiently exact, and that the lead acetates and the gallotannic acid did not contribute anything to the amount of glucose actually present.

The second series was made on a solution containing glucose, 0.5 per cent., pure gallic acid, 1.0 per cent., and pure gallotannic acid, 1.0 per cent. By the ordinary methods of detannization, in one case using normal and in the other case basic acetate, the result for the percentage of glucose came out the same in both cases, 0.52 per cent.

This bears out the previous statement that gallic acid is precipitated by both normal and basic lead acetates in neutral solution, and the error is practically negligible.

The next experiments were made on a similar solution to the above, with the addition of acetic acid. This artificial solution would correspond to an actual water soluble matter solution: Glucose, 0.5 per cent., gallotannic acid, 1.0 per cent., gallic acid, 1.0 per cent., acetic acid, 0.5 per cent. This solution was detannized, and the subsequent operations were carried out as before. The percentage of glucose found when normal acetate was used

Digitized by Google

for detannizing was 0.57 per cent., and with basic acetate 0.54 per cent.

It will be seen that the above is the sort of result that was obtained with actual water soluble matter solutions, the normal giving higher figures than the basic, and both giving too high results. It is evident that the acetic acid prevents the complete precipitation of gallic acid, and that with normal acetate the precipitation is less complete than with basic acetate.

To confirm the above conclusion, the same solution was neutralized by adding caustic potash solution until neutral to phenolphthalein. (The phenolphthalein was used as external indicator and spotted on to a white tile, and the caustic potash solution added to the solution until a drop gave a violet coloration.) It is essential that the solution should not stand when once it has been neutralized by the alkali, otherwise it quickly becomes dark colored and oxidizes. The detannization must take place immediately after neutralization. The results were: Normal acetate, 0.52 per cent. glucose, basic acetate, 0.51 per cent. glucose. It will be seen that this brings down the result to the correct figure. The acid has been neutralized, and it can no longer keep in solution the gallic acid. The gallic acid is precipitated by the acetate, and the correct figures for the glucose are obtained.

The following table shows the results in a condensed form:

Actual solution	Normal lead acetate percentage of glucose found	Basic lead acetate percentage of glucose found
A. 0.50% glucose. 1.00% gallotannic acid..	0.51	0.51
B. A + 1.00% gallic acid.....	0.52	0.52
C. B + 0.50% acetic acid.....	0.57	0.54
D. C neutralized befor detannisation.....	0.52	0.51

In applying these considerations to actual leathers containing glucose, the same kind of result was obtained, but not to such a marked extent. Normal acetate gave higher results than basic, and the neutralization of the solution before detannization lowered the figures for glucose, but not so much as with the artificial solution: *c. g.*, one weighted leather gave the figures:

	Normal acetate		Basic acetate	
	Alone	Netralized before detannization	Alone	Neutralized before detannization
Percentage of glucose	8.7	8.1	7.8	7.3

Digitized by Google

Since the above experiments were carried out, Stiasny and Wilkinson have published a comprehensive paper on the qualitative detection of the different tannins (*Collegium,* 1911, 318-332; this J., 1911, 479). One of the most important reactions therein described is the precipitation with normal and basic lead acetates and is was found that whereas all tannins are completely precipitated by lead acetate in the absence of acid, the precipitation is not complete in presence of acetic acid. The catechol tannins differ in this respect from the pyrogallol tannins; in presence of excess of acetic acid the catechol tannins are not precipitated at all, whilst most of the pyrogallol tannins are precipitated. The important point in the present consideration is that all tannins are not completely precipitated by normal lead acetate in presence of free acid. In a leather analysis, therefore, it may arise, with the use of normal lead acetate, that all the tannin will not be removed in the detannization, and the unprecipitated tannin may reduce the Fehling's solution and produce a higher figure for the glucose. This should be additional argument against the proposal use of the normal lead acetate.

(It will be observed that in the experiment on actual extractive matter from leather, there is nothing to show which of the four results given is nearest to the truth. The A. L. C. A. did not adopt normal lead acetate because it was believed to give perfect results, either in specially arranged tests or in actual practice, but because in the latter case it generally gives a more nearly correct estimate of sugars actually present in the leather than the basic acetate. This approximation to accuracy seems to be due to a balancing of errors.—L. B.)

DEVICE FOR PIPETTING DANGEROUS LIQUIDS.

By L. Balderston.

In analyzing some stale soaks it became necessary to measure accurately 100 cc. of each. To do this using a pipette in the ordinary way is a very offensive task, and a few drops of a stale soak in one's mouth might be a serious matter because of possible disease germs. The device described below worked so rapidly

Digitized by Google

and well that it was thought worth mentioning in the JOURNAL. The same method has since been used in pipetting hydrochloric acid, with equal success.

Connect the pipette to be used with another at least twice as large, by means of a rubber tube slipped over the upper ends of the pipettes. This tube will need to be about as long as the larger pipette. Nearly fill with water a cylinder large enough to hold the larger pipette, and so high that when the pipette is stood in it the top of the bulb comes an inch or two below the top of the cylinder. Now thrust the large pipette into the cylinder of water, allowing the bulb to fill. Place the tip of the other pipette in the liquid to be measured, holding it with the thumb and forefinger grasping the rubber tube rather loosely just above the top of the pipette. Now raise the large pipette, and as the water flows out of it the liquid is drawn up into the other. The large pipette should not be lifted out of the water, but it must be raised far enough for the difference of level between the water in the pipette and the cylinder to be a little greater than the height to which the other liquid must rise. When the measuring pipette is full to the mark or above, grasp the tube above it tightly and lift it out. Adjustment to the mark is easy with a little practice. While the liquid is being delivered, push the large pipette back into the water.

In using a 100 cc. pipette in this way, it is convenient to have its length from tip to mark less than usual; otherwise it is difficult to raise the liquid to the mark, since a 200 cc. pipette from top of bulb to tip is generally not longer than the 100 cc. from tip to mark. We used a cylinder 20 inches deep, a 200 cc. pipette 17 inches from tip to top of bulb, and a 100 cc. pipette 12 inches long from tip to mark. For pipetting smaller quantities it is easy to select a pipette and cylinder long enough to do.

ABSTRACTS.

An Investigation of the Acid Character of Gallotannic Acid. M. A. R. PANIKER and EDMUND STIASNY. *Collegium*, 1912, 9-23. In spite of the large amount of experimental data which has accumulated on the subject of late, the chemical constitution of gallotannic acid is not yet settled in a universally acknowledged way. Dividing the problem into

Digitized by Google

separate parts, the following questions may be regarded as the most interesting:

1. Is gallotannic acid a single body or a mixture?
2. Is gallotannic acid a real acid, viz., containing carboxyl groups?
3. How has the optical activity to be explained?

As to the homogeneity of gallotannic acid we find the view of different authors, assuming that we have to deal with a mixture of allied substances. Walden (*Berichte*, 30, p. 3151, 1897) came to this conclusion when he studied the dialytic behavior of gallotannic acid and the properties of the different products gained by fractional precipitation; he also observed the different optical activity of samples, purified by different methods (compare Rosenheim and Schidrowitz, *Jour. Chem. Soc.*, 73, 885, 1898; Dekker, *Ber.*, 39, 2497, 1906; and Nierenstein, *Chem. Ztg.*, 33, 1909) and explained this fact in the above sense. Aweng (*Revue Intern. falsific*, 11, p. 29, 1898) came to the same conclusion studying the condensation products of gallotannic acid with formaldehyde. In a quite different way, viz., by capillary analytical experiments, Kunz-Krause (*Schweiz. Wochenschrift für Chemie und Pharmacie*, 1898, No. 38) arrived at the same result, finding that a 5 per cent. aqueous solution of pure gallotannic acid gave two distinct capillary zones. And finally we see that Nierenstein (*Berichte*, 38, 3641, 1905; 40, 917, 1907; 41, 77, 3015, 1908; 42, 1122, 3552, 1909; 43, 628, 1910; *Chem. Ztg.*, 31, 72, 1907; 34, 15, 1909) in his interesting papers on the subject explains the properties of gallotannic acid by considering it to be a mixture of digallic acid and leukotannin.

As regards the acid character of gallotannin, expressed by the presence of a free carboxyl group in the well-known Schiff's formula, we find that several authors do not believe in it. Thus Boettinger (*Berichte*, 17, 1503, 1884) found that benzoyl-gallotannin is insoluble in alkali, and Dekker (*Berichte*, 39, 2497, 1906) showed that his acetyl compound of gallotannin could be boiled with great excess of N — NaOH without being dissolved. Dekker therefore argued that no free carboxyl group can be present in the molecule of gallotannin and he finds this assumption confirmed by the work of Walden (*Berichte*, 31, 3170, 1898) who determined the electrical conductivity of gallotannin and who found such very low figures for its affinity-constant that he assumed gallotannin to be of a non-electrolytic nature, the small experimental figures being due to impurities.

In the present paper the question of the acid character of gallotannin is principally dealt with, but there will be some opportunity to touch the question of the homogeneity of this substance.

The determination of the hydrion concentration of gallotannin was carried out by the method of Bredig and Fraenkel (*Zeit. f. Phys. Chem.*, lx, pp. 202-6) which is based on the evolution of nitrogen from diazoacetic ester due to the catalytic influence of hydrions.

$$CHN_2COOEt + H_2O = CH_2OH.COOEt + N_2.$$

Digitized by Google

This method has given very satisfactory and concordant results in determinations of a like nature (Spitalsky, *Zeit. f. Anorg. Chem.*, 54, 265; Bror Holmberg, *Zeit. f. Phys. Chem.*, 62, 726), sufficient to justify its application to the study of the acid character of gallotannic acid or bodies of an allied nature.

Pure water has practically no action on the ester and the reaction is capable of indicating a hydrion concentration varying from 0.00008 mols per liter to 0.0025 mols per liter at 25° without any difficulty in manipulation. In the one case half the amount of the ester used is decomposed in about 4½ hours while in the other in about 9 minutes.

Preparation of Diazo Acetic Ester.—The diazo-ester is prepared from the hydrochloride of glycocollester which is best obtained by the hydrolysis of methylene-amino-acetonitrile ($CH_2:OCH_2CN$) (*Klages B.*, 1903, 36, 1506) produced by the action of KCN on a mixture of formaldehyde and ammonium chloride.

The diazo-ester is obtained in a pure state by adopting the methods of previous workers (Curtius, *Jour. f. prakt. Chem.*, 38, 396; Ernst Muller, *Dissertation*, Heidelberg, 1904; Silberrad, *Trans. Chem. Soc.*, 1902, 600). A detailed description of this method is further given by Fraenkel (*Zeit. f. physik. Chem.*, 40, 202).

A cold saturated solution of 50 grams of pure hydrochloride of glycocoll ester is shaken up with a concentrated solution of 25 grams of sodium nitrite, and the diazotized product removed with pure ether after the addition of a few drops of 10 per cent. H_2SO_4. On further acidification and shaking with pure ether more of the diazo-ester could be obtained. The ethereal solution is then neutralized with a weak solution of sodium carbonate, carefully washed with small quantities of pure water and finally dried over fused calcium chloride. The major portion of the ether is next distilled off in vacuo at the ordinary temperature and the residue subjected to distillation in steam under diminished pressure. As in an alkaline medium, the distillation is quite safe without fear of an explosion taking place, a few grams of pure barium hydroxide crystals are added to the residue before distillation. At a pressure of about 20 mm. the ester mixes with water vapor and distils over at a temperature of 30° C. To avoid loss of ester, the receiver should be cooled in a strong mixture of ice and calcium chloride.

The distillate should be carefully separated from the upper aqueous layer and dissolved in pure ether (purified over KOH and distilled over sodium wire). After dehydration over fused calcium chloride for several days, the ether is evaporated in vacuo and the residue finally distilled over freshly burnt calcium oxide under diminished pressure. Under a pressure of 50 mm. of mercury, the ester distils over at a temperature of 45 to 50° C. and is collected in a vacuum tube kept cooled in ice. Yield about 20 to 25 grams on the average. If kept in a cool place well corked and standing over cold water in the dark the ester is found to keep for at least a month without decomposition. The purity of the

Digitized by Google

ester is tested from time to time by performing blank experiments with pure water alone, and if any appreciable amount of nitrogen is registered in the nitrometer, the ester is redistilled over freshly burnt quicklime as stated above and again tested for purity. Sometimes this distillation alone would not be sufficient and in such cases it has to be purified over barium hydroxide by distillation in steam and further over burnt lime as described above.

Apparatus and Modus Operandi.—The reaction was carried out in a Walton flask (for description of the apparatus see *Zeit. f. Phys. Chem.*, 47, 185) connected to an ordinary nitrometer, graduated to 0.2 cc. and fitted with a water jacket. Twenty cc. of the solution containing the substance under examination were pipetted into the Walton flask and 0.2 cc. of the ester weighed out into the small tube which was then made to rest in the neck of the flask on the tip of the glass rod passing through the side tube. The flask was then closed by a tight fitting rubber stopper carrying the capillary tube which connects it to the nitrometer. When the flask had stood about ten minutes in the thermostat, the capillary tube was connected to the nitrometer by a piece of rubber tubing and tightly fixed by copper wire. The level of water in the nitrometer should previously be adjusted with care, and any correction required for a change of pressure brought about by the connection of the apparatus should also be allowed for. The experiments were performed at a temperature of the thermostat varying from 25° to 25.5°. The tube containing the ester was then allowed to drop into the solution, the time carefully noted, and shaking started simultaneously. When the reaction had proceeded for a time (usually from 10 to 15 minutes) and the solutions mixed thoroughly, the volume of nitrogen evolved was noted at fixed intervals and the temperature of water in the nitrometer jacket observed at the same time. The barometer is noted both at the commencement and end of the reaction. The volume of nitrogen generated within a given interval of time was reduced to N.T.P. The velocity of the reaction is then calculated from the formula:

$$k = \frac{1}{0.4343t} \cdot \log \frac{a}{a - x},$$

where a = the total volume of nitrogen corresponding to a given concentration of the ester and x = the volume of nitrogen evolved in time t.

To insure the purity of the water used for the following experiments, ordinary distilled water was redistilled thrice through Jena glass and stored away in a Jena flask. It should further be freed from carbonic acid by aspirating through it air drawn through (1) concentrated sulphuric acid, (2) a series of U tubes containing fused calcium chloride and soda lime and (3) finally filtered through cotton wool packed in a long tube.

Our first experiments were conducted in a glass flask, but it was soon evident that where weak organic acids are used as catalysers the velocity constant is affected by the alkalinity of the glass, the concentration of

Digitized by Google

hydrions being reduced to an appreciable extent. Pyrogallol, phenol, and boric acid give only traces of nitrogen after the reaction had proceeded for over 17 hours. Gallic, proctocatechuic, β resorcylic, and salicylic acids gave the following values of k:

Gallic acid	0.01337
Protocatechuic acid	0.01122
β Resorcylic acid	0.04999
Salicylic acid	0.0751

These values are of the same order as those found by the electrical conductivity method, but the figures are not exact as the value of k dropped with increase of time, since the alkalinity of the glass produced a gradual neutralization. The negative result in the case of the weak electrolytes, phenol, boric acid, etc., is also to be attributed to this cause. A quartz flask was therefore used for later experiments and the results have proved it a very satisfactory substitute for glass. Fraenkel uses a platinum flask for his experiments and Spitalsky finds paraffinized glass equally efficient. Before and after any particular experiment the ester is tested for purity, using 20 cc. pure water and 0.2 cc. ester, and in all cases where more than 0.6 cc. nitrogen are evolved after 20 hours the ester has been purified by distillation for use. The following experinemts have all been performed in the silica flask.

Experiment 1.—Catalyser: Pyrogallol (0.001 mol.). Concentration of ester 0.2018 gr. in 20.2 cc. Mean temp. nitrometer 11°. Aqueous tension 9.9 mm. Barometer 759.5 mm. $a = 39.65$ cc. Mean value of $k = 0.0000810$.

Experiment 2.—Catalyser: Boric acid (0.0008671 mol. in 22 cc.). 20 cc. of ester solution + 2 cc. of boric acid solution. Concentration of ester 0.20352 gr. in 20.2 cc. Mean temp. nitrometer 11.5°. Aqueous tension 10.2 mm. Barometer 752.1 mm. $a = 40.0$ cc. Mean value of $k = 0.000065$.

Gallotanic Acid.—A series of experiments were made with gallotannic acid and all duplicates have shown good concordance. The experiments performed in the glass apparatus are not given here as they are not quite reliable. Starting from Kahlbaum's purest sample of tannic acid, different methods of further purification were adopted and the products tested in different stages as detailed below.

Methods of Purification Employed.—Sample used: Kahlbaum's Extra Pure Tannic Acid.

Method I: Fifty grams of Kahlbaum's extra pure tannic acid were dissolved in 500 cc. water and precipitated by means of a saturated solution of pure sodium chloride. The precipitate was repeatedly washed on the filter with the salt solution again dissolved in a small quantity of water and salted out. This salting out process was repeated half a dozen times and the product finally dried in vacuum oven at a low temperature. The dried mass was then extracted with freshly distilled methyl acetate, filtered and the filtrate evaporated in vacuo at the laboratory temperature and dried thoroughly free from all traces of the solvent.

Digitized by Google

The sample so obtained was by no means free from traces of gallic acid which are invariably carried down with the precipitate during the salting-out operations. (See Experiment 3.) As the rate of decomposition of the ester is directly proportional to the concentration of hydrions in solution, the specific influence of the hydrions must be a constant factor. In other words, $k/C_{\dot{H}}$ is a constant quantity; the value of this constant has been determined by Fraenkel (*loc. cit.*). For aqueous solution $k/C_{\dot{H}} = 38.5$. $C_{\dot{H}}$ (calculated from the above equation) $= 8.5 \times 10^{-5}$.

Experiment 3.

Catalyser: 0.322 g. Gallotannic Acid, purified by Method I.
Concentration of ester 0.1936 gr. in 20.2 cc.
Mean temp. Nitrometer 11°. Aqueous tension 9.9 mm.
Barometer 755.7 mm.
$a = 38.04$ cc.

t (minutes)	x cc.	x^1 cc.	$a-x^1$	k
20	1.9	1.79	36.25	0.003213
25	2.6	2.45	35.59	0.003329
30	3.2	3.02	35.02	0.003297
40	3.8	3.58	34.46	0.003287
60	5.0	4.72	33.32	0.003312
80	7.3	6.89	31.15	0.003330
100	9.5	8.96	29.08	0.003357
180	11.5	10.85	27.19	0.003358

Mean value of $k = 0.003277$.

Method II: (Rosenheim and Schidrowitz *Trans.*, 73, 878.) Fifty grams Kahlbaum's tannin were dissolved in a small quantity of pure acetone. On the addition of pure ether, a white amorphous precipitate was formed which soon settled down as black resinous matter. On the addition of a small quantity of water to the filtrate, two layers were formed. The heavier syrupy layer was separated and repeatedly shaken out with pure ether till the ethereal layer remained colorless. On the addition of more water, three layers were formed and the lowest layer containing the least amount of gallic acid was removed and again shaken out with ether several times till the ethereal layer gave but a faint test with potassium cyanide (Young's reaction. *Chem. News,* 1883, 48, 31). The emulsion was allowed to separate (usually from 24 to 48 hours) and the lower layer evaporated on the water-bath, dried in vacuo and desiccated over sulphuric acid in a vacuum dryer protected from light. The above purification was repeated several times and the resulting substance tested for acidity in successive stages of purification. This method, depending as it does on the phenomenon of distribution of a substance between two solvents, is by no means a perfect one. The small amount of gallic acid which is always left behind in the purified sample introduces a greater variation in the degree of acidity than in the values obtained by the authors above referred to for the specific rotatory power of the substance. (See Experiments 4, 5, 6 and 7.)

Digitized by Google

Experiment 4.—Catalyser: 0.322 gr. gallotannic acid, Method II, first purification. Concentration of ester 0.2036 gr. in 20.2 cc. Mean temp. nitrometer 11°. Aqueous tension 9.9 mm. Barometer 750.5 mm. $a =$ 40.01 cc. $t = 25$-1140 min. Mean value of $k = 0.004417$. $C_H^{\cdot} = 11.47 \times 10^{-5}$.

Experiment 5.—Catalyser: 0.3383 gr. gallotannic acid; Method II, second purification. Concentration of ester 0.2123 gr. in 20.2 cc. Mean temp. nitrometer 11°. Aqueous tension 9.9 mm. Barometer 757.2 mm. $a = 41.72$ cc. $t = 20$-315 min. Mean value of $k = 0.002398$. $C_H^{\cdot} = 62. \times 10^{-5}$.

Experiment 6.—Catalyser: 0.3289 gr. gallotannic acid; Method II, third purification. Concentration of ester 0.2106 gr. in 20.2 cc. Mean temp. nitrometer 11°. Aqueous tension 9.9 mm. Barometer 762 mm. $a =$ 41.39 cc. $t = 15$-315 min. Mean value of $k = 0.001980$. $C_H^{\cdot} = 51 \times 10^{-5}$.

Experiment 7.—Catalyser: 0.3244 gr. gallotannic acid; Method II, fourth purification. Concentration of ester 0.2050 gr. in 20.2 cc. Mean barometer 749.6 mm. $a = 40.28$ cc. $t = 30$-360 min. Mean value of $k = 231 \times 10^{-5}$. $C_H^{\cdot} = 6 \times 10^{-5}$.

Method III: Neutralization by means of sodium bicarbonate and extraction with ethyl acetate. (This method was suggested to us by Mr. A. G. Perkin, to whom we are indebted for the great interest he took in this work.) The commercial product was first purified from all resinous and coloring matter by repeatedly shaking out the acetone solution with ether (see Method II) and the residue dried as before. The product so obtained was dissolved in a small quantity of water. To avoid the presence of any normal carbonate, a current of CO_2 was passed through a saturated solution of sodium bicarbonate for about 20 minutes. The aqueous solution of the tannin was similarly freed from oxygen and neutralized with the bicarbonate solution

1. Till faintly alkaline to litmus. The solution was then shaken out three times with freshly distilled ethyl acetate. The extract so obtained was washed with small quantities of water till free from traces of alkali, and concentrated in vacuo at the ordinary temperature and precipitated by means of pure dry benzene. The white precipitate so obtained was boiled with benzene to remove traces of the ester, filtered and finally dried in the vacuum oven for four hours. The acidity of the product was then tested. The above purification was then repeated using more of the bicarbonate solution

2. Till the liquid was more alkaline than in the previous case. The product so obtained was tested for acidity. Repeating the process of purification for a third time, the aqueous solution of the substance was

3. Finally precipitated with the bicarbonate solution and extracted as before. The product was again examined as in the two previous cases. The mother liquor obtained after precipitation with the bicarbonate solution was

4. Partly neutralized with hydrochloric acid and extracted with ethyl

Digitized by Google

acetate, washed, concentrated and finally precipitated with benzene. In the place of a white amorphous precipitate obtained in the last case, a dark viscous mass was thrown down which when dried was greyish white in color. The acidity of this product was also noted. Owing to the insolubility of sodium gallate and other allied salts in ethyl acetate, this method is an excellent means of purifying gallo tannic acid. The products so obtained are invariably free from even traces of sodium. (See Experiments 8-11.)

A COMPARATIVE REVIEW OF THE DIFFERENT METHODS OF PURIFICATION OF GALLOTANNIC ACID.

a. Method I (Precipitation by means of NaCl) is not sufficient to get rid of all gallic acid from the commercial sample. A sample which was salted out 24 times still gave, after extraction with ethyl acetate or alcohol, a faint gallic acid reaction with KCN. This fact is clearly shown by the high values obtained for k and C_H.

b. Method II (Unequal distribution of gallic and gallotannic acid in ether and acetone) is a tedious one and we can never, even from theoretical considerations, get a sample completely free from gallic acid. It could be seen from the tables that as the purification proceeds the velocity constant and consequently the hydrion concentration both diminish and approximate to a constant value.

c. Method III (Insolubility of sodium gallate in acetic ether) is by far the best which has been employed for the complete separation of gallic acid impurity from gallotannin. Unlike Method II, even the first fraction is so thoroughly free from gallic acid that we might with sufficient justification state that the Hion concentration 5.8×10^{-5} (see table) is outside the influence of gallic acid.

Conditions which Govern the Progress of the Reaction.—The temperature coefficient of the reaction, judging from analogy drawn from similar catalytic reactions, is by no means negligible. A difference of 0.25 to 0.5 which the thermostat had shown during the course of some experiments is perhaps sufficient in the majority of cases to account for the deviation which in certain cases k exhibits from its mean value. The rate of evolution of nitrogen as measured by the nitrometer readings is considerably influenced by the character of the solution as well. When it is of a colloidal character as with gallotannic acid solutions, a considerable amount of the gas is retained on the surface of the solution in the reaction flask, which consequently escapes measurement and leads to a variation in the observed rate of the reaction.

Experiment 8.—Catalyser: 0.3347 gr. gallotannic acid; Method III, first purification. Concentration of ester 0.2111 gr. in 20.2 cc. Mean temp. nitrometer 11°. Aqueous tension 9.9 mm. Barometer 740.7 mm. $a =$ 41.48 cc. $t =$ 20-180 min. Mean value of $k = 0.002236$. $C_H = 5.8 \times 10^{-5}$.

Experiment 9.—Catalyser: 0.3013 gr. gallotannic acid, Method III, second purification. Concentration of ester 0.2079 gr. in 20.2 cc. Mean

Digitized by Google

barometer 762.5 mm. $a = 40.85$ cc. $t = 20\text{-}376$ min. Mean value of $k = 0.001478$. $C_H = 3.8 \times 10^{-5}$.

Experiment 10.—Catalyser: 0.3159 gr. gallotannic acid; Method III, third purification. Concentration of ester 0.2034 gr. in 20.2 cc. Mean barometer 764.7 mm. $a = 39.97$ mm. $t = 15\text{-}385$ min. Mean value of $k = 0.001121$. $C_H = 2.9 \times 10^{-5}$.

Affinity Constant and Optical Activity.—No proportionality seems to exist between the specific rotatory power of the substance and its velocity constant. This relationship seems to depend largely on the method of purification employed, and is also governed by the amount of gallic acid impurity left in the sample. Purification by Method II, based on the work of Rosenheim and Schidrowitz gives a substance with constant values for k and $[\alpha]_D$ and judged alone it would seem to indicate that gallotannic acid is an acid of constant rotatory power and of definite acidity. When we proceed to purify the same substance according to Method III, a perceptible increase in the value of $[\alpha]_D$ manifests itself as the value of k drops down with the order of purification. This would naturally indicate a partial differentiation of the proximate constituents. Method III has already been stated to yield a product free from gallic acid. As could be gathered from the figures given in the table the value of $[\alpha]_D$ in this case does not come up to the amount shown by any of the purified samples under Method II. Further, the acidity of the products in this case approximates to a minimum value. Moreover, by extracting the neutralized product from the mother liquor according to Method III, we get a body which gives a velocity constant with almost double the value obtained in the case of the third sample (Method III_3). If these be two different chemical individuals, then naturally the one must be twice as strong as the other in its chemical affinity. These facts do not permit us to conclude that we are here dealing with a homogeneous substance.

Experiment 11.—Catalyser: 0.3241 gallotannic acid; Method III, mother liquor. Concentration of ester 0.2012 gr. in 20.2 cc. Mean barometer 747.6 mm. $a = 39.53$ cc. Mean value of $k = 0.0b2142$. $C_H = 5.6 \times 10^{-5}$.

The following table is a summary of the above experiments where the values of k are compared with the spec. rotatory power of each sample.

To compare the degree of dissociation of gallotannic acid with that of any other weak organic acid like gallic, we should naturally have some idea of the molecular weight of the substance in aqueous solution. According to Ssabanejew, gallotannic acid has a molecular weight 1322 in water, but we know well enough that this number has no molecular significance in as much as the ordinary osmotic methods cannot be used for the determination of molecular weight of substances in a colloidal solution. The fact that we are able to divide tannic acid into two parts by saturating the solution with sodium bicarbonate, the one part being soluble in ethyl acetate while the other forms a sodium salt which on acidification is capable of being extracted with ethyl acetate, points to

Digitized by Google

Purification Method	Order	Concentration	K	C_H	$[L_D]_{17^0}$	Remarks
Method I	—	0.322 gr. in 20.2 cc.	328×10^{-5}	8.5×10^{-5}	—	Rich in gallic acid
Method II	1st	0.322 gr. in 20.2 cc.	442×10^{-5}	11.5×10^{-5}	$+73.29^0$	Rich in gallic acid
Method II	2d	0.3383 gr. in 20.2 cc.	240×10^{-5}	6.2×10^{-5}	$+72.12^0$	Contained traces of gallic acid
Method II	3d	0.3289 gr. in 20.2 cc.	198×10^{-5}	5.1×10^{-5}	$+72.37^0$	Seems free from gallic acid
Method II	4th	0.3244 gr. in 20.2 cc.	231×10^{-5}	6.0×10^{-5}	$+70.90^0$	Seems free from gallic acid
Method III	1st	0.3347 gr. in 20.2 cc.	224×10^{-5}	5.8×10^{-5}	$+56.76^0$	Free from even traces of gallic acid
Method III	2d	0.3013 gr. in 20.2 cc.	148×10^{-5}	3.8×10^{-5}	$+64.72^0$	Free from even traces of gallic acid
Method III	3d	0.3159 gr. in 20.2 cc.	112×10^{-5}	2.9×10^{-5}	$+69.60^0$	Free from even traces of gallic acid
Meth. III; extracted from Mother liquor (III_4)		0.32408 gr. in 20.2 cc.	214×10^{-5}	5.6×10^{-5}	$+65.10^0$	Free from even traces of gallic acid

Digitized by Google

the fact that we have here to deal with a mixture of two or more substances of different degrees of acidity. This view is favored by the fact that the substance extracted direct after neutralization with sodium bicarbonate is only half as acid as that which is set free on acidifying the sodium salt in solution. The difference in the values of k and $[\alpha]_D$ shown by different samples purified after different methods also supported this view. Another observation may also be mentioned although it still wants further investigation. If the white amorphous precipitate obtained by salting out the solution of gallotannin is dissolved in absolute alcohol and treated with an absolute alcoholic solution of potassium acetate, a precipitate is formed, which in similar cases has been shown by A. G. Perkin (*Trans. Chem. Soc.*, 1908, Vol. 83, p. 129) to be the potassium salt of the acid or an oxonium salt. This precipitate was washed with absolute alcohol and treated with pure ethyl acetate to remove traces of any free gallotannic acid. It was then filtered, dried and analyzed. The following analytical figures were obtained which when calculated seem to agree with the monomolecular formula $C_{14}H_9O_9K$ for the potassium salt:

0.4383 gr. of the substance yielded on ignition with H_2SO_4
0.1032 gr. of K_2SO_4

K_2SO_4 calculated for $C_{14}H_9O_9K$ ..... 0.1059 gr.
K_2SO_4 found ..... 0.1032 gr.

The optical inactivity of this potassium salt and the optical behavior of gallotannic acid, prepared from the former, will form the subject of a special paper, which, we hope, will throw some light on the constitution of gallotannic acid.

SUMMARY.

The foregoing experiments seem to be in favor of the view that gallotannic acid is a mixture of two or more chemical individuals, possibly of an allied character (compare Kunz-Krause, Walden, Aweng, Nierenstein). On the other hand our observations do not agree with the view of Boettinger, Walden and Dekker that gallotannic acid has no free carboxyl group, as the affinity constant found by us is distinctly of a higher order than those for phenols.

The Mangrove Bark of North Queensland and the Manufacture of Mangrove Cutch. F. A. Coombs and G. H. Russell. *J. Soc. Chem. Ind.*, 31, 212-15, Mar. 15, 1912. Mangrove grows in profusion on the northeastern coast of Queensland. Seven species are mentioned, of which the most important are *Rhizophora mucronata, Bruguiera gymnorrhiza* and *Ceriops candolleana*, whose bark makes 10 to 23 per cent. of the total weight of the stem. The cost of collecting is small. The bark ranges from ¼ to 1 inch in thickness, being soft when stripped, and containing much moisture. It must be cured under cover, as direct sunlight while curing darkens the color, as does exposure to wet. In the making of extract the bark is rather coarsely ground, to permit the leach water to percolate freely. In leaching, any one of the three customary methods may be

Digitized by Google

employed, diffusion, decoction, or percolation. The authors regard the last as the best. Boiling water is sprinkled on the top of the leach and drawn off from a chamber under the false bottom. In the experiments of the authors 6.85 per cent. of tannin remained in the spent bark. (It is not stated whether or not this is on the basis of the new bark.) The average total tannin is about 39 per cent. If the extract is to be used as a dye, liquor obtained by the methods mentioned is satisfactory, but if a tanning extract is desired, the liquor is decolorized by heating with blood albumin before concentration. The extract prepared by the authors in the laboratory of Sydney Technical College, was solid, containing about 12 per cent. water, 68.5 per cent. tannin and 17.3 per cent. non-tans. L. B.

White Pigments for Leather. ALAN A. CLAFLIN. *S. and L. Rep.*, Mar. 21, 1912. Leather must be whitened by covering up its original color. The old recipes precipitated sulphate of lead on the fiber by saturating the leather with sugar of lead and dipping in a solution of sulphate of soda. This process is rather costly and the sulphate of lead is poisonous. This method is practically obsolete. Barium sulphate is used in the form of the finely ground natural product or as a precipitate in paste form ("blanc fixe") or is precipitated on the fiber. The first is apt to be somewhat gritty, but is the least expensive form. These compounds are heavy and not very opaque, so that a good white can be produced only by using a relatively large quantity. Carbonate of magnesia is very opaque and very light. Its small resistance to acids would be an objection for some uses. Talc is much used. Italian talc is white, slippery, and free from grit. The best grades of North Carolina talc are nearly as white, and half as expensive, but less slippery than the Italian. The same is true of those from New York. Vermont talcs are as slippery as the Italian but are somewhat gray. Massachusetts produces some good talc. White clay is used in filling white leathers under the names China clay and pipe clay. The latter is made by grinding and bolting China clay. Whiting is the natural calcium carbonate ground and bolted. It is liable to be gritty and lacks the lubricating property of talc and clay. It is also attacked by acids. L. B.

Notes with Regard to Tanning Extracts. *Shoe and Leather Reporter.* March 21, 1912. One advantage of extracts over raw materials is the saving in freight charges and in space for storage at the tannery. The trouble and expense of leaching are saved, and liquors of any strength may be prepared very quickly. The best practicable leaching leaves in the spent bark often as much as 10 per cent. of the tannin originally present. Not all the tannin shown by analysis may be soluble in the strong liquors of the tannery, since the analysis solutions are very dilute, but with most kinds of extracts nearly all the tannin present is available for use. The most notable exception is ordinary solid quebracho. The author suggests that in valuing this material an important test is to see how much material soluble in liquor of analytical strength is thrown

Digitized by Google

out of solution in a liquor of the strength to be used in the tannery. If the extract is dissolved in hot liquors, the amount of tannin thrown out in cooling afterward is sometimes less than that lost by dissolving in cold liquors. In the case of sulphited quebracho there is no appreciable difference. The temperature at which the extract is dissolved should be high enough to dissolve all, or as much as possible of the extract. This temperature should not be exceeded, as the color is apt to be darkened.

The use of extracts has made possible much more rapid tannage than could be done with oak bark or other old-time materials. With oak bark alone two years was sometimes required, while it is possible to tan heavy leather with extract in not much more than two weeks. This difference is due in large part to the greater strength of the liquors now used. The strongest bark liquor seldom reached 40° barkometer, while extract liquors may be used whose strength is 150°. The more rapid tanning produces a leather containing a larger proportion of material that can be washed out. During the first few days of tannage, nearly all the tannin absorbed combines with the hide fiber but in the later stages a large part of what is absorbed may be washed out again. After the hides are colored through, the strength of the liquors may be rapidly increased without danger of "case-hardening." The stronger the liquors in these stages, the larger will be the amount of tannin absorbed but not combined. The quality of the rapidly tanned leather for soles is therefore inferior to that of the leather produced by the old-fashioned slow tannage. In the latter a large proportion of the material deposited in the leather is the "bloom," an insoluble substance, resulting from changes in the liquors which require time. In the shortened process the number of hides which can be handled in a given space is larger, and it is easier to follow the requirements of the market. L. B.

The Livache and Other Tests for Linseed Oil and Its Adulterants. J. S. LIVERSEEGE and G. D. ELSON. *J. Soc. Chem. Ind.*, **31**, 207-8, Mar. 15, **1912.** Of methods for testing the drying power of oils, that of Livache (*J. S. C. I.*, 5. 494, 1886) has been used most. It employs lead, manganese nitrate, and lead oxide. Walker (Bulletin 109, Bureau of Chem., U. S. Dept. Agr.) has devised an improvement but in using this method the authors found difficulty in securing good duplicates. They obtained concordant results by the process which is described below. Litharge is finely powdered and spread in a thin layer over night at 20°-22° C. Its weight should then be constant. Ten g. are placed in a flat-bottomed German silver dish of 3 inches diameter and 1 inch depth. The whole is weighed and 0.7 to 0.9 g. oil added. After weighing, 5 cc. methylated ether is added; and the dish rocked so as to spread the contents uniformly. The dish is then kept at 20-22° C. for several days, and weighed at suitable intervals. The ether volatilizes completely in half an hour. The non-volatile residue from this source must be reckoned with. It does not usually exceed 3 mg. Gains are expressed as percentages of the amounts of oil taken. Five samples of genuine raw linseed oil

Digitized by Google

showed in two days gains of 17.2, 16.8, 17.4, 17.0 and 17.4 per cent. They then began to lose, and by the 14th day the average of excess above the original weight was only 15.9 per cent. Boiled oil reached a maximum of 14.1 per cent. gain in 1 day. and then began to lose. Soja bean oil gained 8.6 per cent. and cotton-seed 6.6 per cent.; time two days. Rape and peanut oils gained 2.5 per cent. and olive oil about 1 per cent. in two days. The last three continued to gain up to 21 days, final gains being 5.7, 4.1 and 3 per cent. respectively. Whale oil gained 6.4 per cent. and seal oil 4.9 per cent. in two days. Resin oil gained 9.9 per cent. in two days and 19.4 per cent. in 13 days In oils of the same class, the iodine value and oxidation value are pretty closely proportional. After treatment with alcoholic potash or soda, the addition of water gives a clear solution with raw linseed oil, or slightly turbid with boiled oil. The presence of small quantities of unsaponifiable matter causes a very turbid solution. L. B.

Blast on Sumac Skivers. *Leather World,* 4, 220. The following precautions are suggested by the Light Leather Federation, in a recent circular letter to the fell-mongers: (1) Clean all soaks and lime pits at frequent intervals; dirty soaks and stale limes result in serious damage to pelts. (2) Goods that have been painted with lime and sulphide of sodium should immediately after pulling be washed in water before being placed in lime. Under no conditions should goods be left lying about in the pulling shop, but should be removed as quickly as possible and placed in lime. (3) Remove all "lime grounds" from bottom of pits before making up "gathering limes." (4) See that the lime is well slaked before use (say 3 days), so as to ensure that it is perfectly cold before being put in the pit, or being used for painting. (5) Pass all slaked lime through a very fine sieve of about 16 mesh. Throw away the lime that will not pass through. (6) All pelts should be kept covered when drawn or when waiting for pitting, or loading into vans. First place some goods flesh down on the floor of the van or truck, which should have been previously brushed and made clean, and covered with clean straw. and then cover over the pile with skins placed flesh side upwards; these in turn should be covered with clean bags or sacking which have been previously wetted in lime liquor, so as to protect the goods from the sun and air. (7) The bags or sacking should be well washed before use, or otherwise there is liability of the goods becoming stained. L. B.

Lactic Acid Bacillus; Influence of Putrid Gases on. A. Trillat. *Comptes rend.,* 1912, 154, 372-374. Strips of paper moistened with suspensions of various cultures of the lactic acid bacillus were exposed, under similar conditions, to the gases arising from decomposing meat broth. After several hours' exposure the papers were transferred to vessels containing sterilized milk. The quantities of acid formed after six hours were in many cases 2-3 times those found in control tests carried out with bacilli which had been exposed only under ordinary atmospheric conditions. The air in proximity to soil containing humus

Digitized by Google

was found to have a similar invigorating influence on the bacillus. Carbon dioxide or ammonia is not responsible for this action, but probably other volatile substances produced by the decomposition of organic matters are concerned. Prolonged exposure to the putrid gases destroys the bacillus. —J. H. L. in *J. S. C. I.*

Lactic Acid Fermentation; The Chief Phases of and Their Practical Importance. M. GRIMM. *Zentr. Bakt. u. Parasitenk.*, 1911, II. Abt., 32, 65-70. *Chem. Zentr.*, 1912, 1, 511. Lactic acid fermentation with pure cultures of *Bact. acidi lactis* at 35° C. can be divided into four distinct phases. In the first phase, that of habituation, which lasts about 4½ hours, a great increase of the number of organisms takes place, but no production of acid. The second phase lasts about 12 hours and is characterized by a progressively increasing vital activity of the bacteria, the optimum being attained at about the fourteenth hour from the beginning of the first phase. The third phase which lasts about 16 hours is characterized by decreasing vital activity or acid-producing power. In the last phase the bacteria lose their power of producing lactic acid. If the physiological power of pure cultures of *Bact. acidi lactis* is to be maintained, they must be re-inoculated during the second phase mentoined above.— A. S. in *J. S. C. I.*

Chamois Leather. ANON. *Hide and Leather*, April 6, 1912. In England thousands of sheepskins are split on a machine, leaving two separate parts known to the trade as skivers and fleshers. The skivers or grains are tanned in a vegetable tannage and finished for hat sweats, pocket-book leathers, etc. The fleshers are tanned in oil for chamois leather. After splitting, the fleshers are drenched in a bran drench to soften them and also to kill the lime. After drenching, the fleshers are placed in a centrifugal drum to remove all possible moisture.

Here, in this country, the fleshers are placed in the stocks and fish oil is added from time to time until all parts of the fleshers are thoroughly impregnated with the oil. Care should be taken in the first milling that all parts of the skin receive the oil, for if any spots remain unoiled it is almost impossible to tan these spots afterwards. In stocking the skins, heat develops, and when a certain temperature is reached it is necessary to remove all the skins from the stocks and spread them on the floor to cool. After cooling, the skins are again placed in the stocks and the process is repeated until a thorough oxidization takes place.

The tanned skins are now placed in a bath of warm water and left for a few hours, when they are pressed under a hydraulic press to remove the oxidized oil. The residue is the true moellon degras and is largely used for fat-liquoring fine leather. The remaining oil is removed by washing the stock in soda ash and water, leaving what is known as soda soap. By means of an acid the grease is separated, giving a cheaper product of degras.

The skins are now bleached by spreading them in a sunny place, wetting them from time to time to help bleaching. A process used for bleaching

Digitized by Google

chamois leather is to first use permanganate of potash followed by a bath of bisulphate of soda or sulphurous acid.

Determination of Acids in Tan Liquors. GEORGE GRASSER. *Collegium*, 1912, 57-8. Simand-Kohnstein's method gives the best results, but being gravimetric often takes more time than practicable. Proctor's useful titration with lime water, depending upon turbidity for end-point, fails with pine liquors since they become turbid even in absence of acids. The author has found a sucessful indicator in rosolic acid, first removing the tannin by gelatine. Ten to thirty cc. of the liquor are mixed with 25 cc. of a gelatine solution containing 4 gms. gelatine, 25 gms. salt, 100 cc. H_2O; 10 0 cc. more H_2O are added and the whole heated with stirring on the water bath until the separation takes place (about 40-45° C.). Prolonged or high heating should be avoided. After filtration through loose cotton the titration is carried out in a porcelain dish with N/2 NaOH till the indicator darkens to orange. For control if desired, the slight excess may be titrated back to yellow with HCl.

CHECK ANALYSES.

Simand-Kohnstein	Spot, litmus paper	Rosolic acid
0.26	0.28	0.28
0.30	0.32	0.32
0.22	0.24	0.24
0.33	0.36	0.36
0.50	0.54	0.54
0.39	0.42	0.42
0.45	0.46	0.48

W. J. K.

Determination of Mineral Oil in Olein. W. N. CHERCHEFFSKY. *Les Mat. Grasses*, 1912 [5], 1595-8. According to the customs tariff, all oils containing 50 per cent. or more unsaponifiable are rated as mineral; for example, a pure olein adulterated with 40-45 per cent. mineral oil would be cleasse das an animal fat, the same as tallow and lard, while a normal suint olein containing 52-53 per cent. unsaponifiable would be classed as mineral. It seemed desirable to the author to distinguish mineral oils from the unsaponifiable substances of olein. He employs his original method of determination of temperature of turbidity in presence of selected solvents as described in above journal, 1910, 1911. On the basis of experiments with known mixtures (quoted in detail) he concludes that the temperature of turbidity with glacial acetic acid varies proportionately to the amount of mineral oil mixed with a suint olein, affording an approximate determination. Analogous results are obtained with anilin which may be used as a check.

The usual analytical constants of the materials experimented with were:

	Sp. gr.	Acid No.	Sapon. No.	Iodine No.	Per cent. upsapon.
Suint olein	.905	100	107	47	39
Soap olein	.005	179	203	78	0.7
Distilled olein	.905	149	188	78	5.7

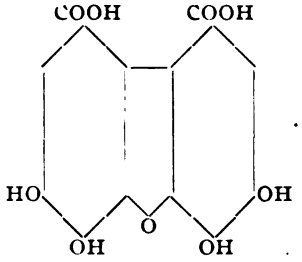
Digitized by Google

The summary of the turbidity temperatures with various oleins:

	Glac. acetic acid	Aniline
Suint olein (40 per cent. unsaponifiable)	29-38	16-21
Soap olein + mineral oil to 40 per cent. unsaponifiable	57-89	36-62
Distilled olein + same	58-93	44-66

Knowing the amount of unsaponifiable one can with the aid of above table conclude with certainty if a mineral oil be present. W. J. K.

The Constitution of Tannin. M. NIERENSTEIN. *Ann. der Chem. u. Pharm.* [386], 318. The author has prepared and examined several well marked tetra substituted derivatives of his purpurotannin (produced by oxidation of leucotannin), including the methyl ether, the benzoyl and acetyl compounds. He now assigns to purpurotannin the constitution:



By reduction with hydriodic acid, biphenylene oxide was produced. The above formula does not harmonize with the formation of naphthalene by distillation with zinc dust which the author previously assumed. He has now repeated these experiments and concludes the distillation product to be instead biphenylene, $C_6H_4:C_6H_4$ (ortho-ortho), on the basis of a combustion and melting point determination. W. J. K.

Tanning Materials and Extracts and Their Technology. LEOPOLD POLLAK. (Address before Austrian Society for Promotion of Chemical Industry.) *Collegium*, 1912, 59-72. Nierenstein defines a tanstuff as possessing an astringent taste and constricting effect upon the mucous membrane; it is soluble in alcohol or water, pptd. by ether, gives a dark colored compound with alkali which further blackens in the air, ppts. albumen, alkaloid and some salts and finally (characteristic) ppts. gelatine and gives blue-black to green coloration with ferric salts. Other phenols besides tannin may, however, give the iron reaction. The chemical constitution of the tannins, although investigated to some extent has little bearing upon their industry. The division, according to their decomposition reactions, into catechol and gallic acid tannins, has use for the tanner. The first deposit ellagic acid (bloom) upon the leather, the second separate the insoluble phlobaphenes (reds). Among the so-called non-tans, found in the natural materials, saccharine substances or glucosides are important, as they yield acids useful during the tannage. Jedlicka (abstract, this JOURNAL, 1909, 162) studied these in oak-wood extract

Digitized by Google

and the author has obtained similar results with chestnut extract. He (the author) found 3.5 to 6.5 per cent. sugar directly present and obtained by hydrolysis of the non-tans 2.5 to 6.5 per cent. and by hydrolysis of the total extract 0.5 to 4.5 per cent. additional, depending upon factory conditions. The amount of direct sugar increases with too hot an extraction and the sugar by hydrolysis of non-tans lowers. A well cleared extract gives but little additional sugar by hydrolysis of total extract, which would indicate that this third sugar number comes from hydrolysis of suspended matter. The series of liquors in an extraction battery gave regular increases in direct sugar (1), decreases in sugar by hydrolysis of non-tans (2), and a constant amount by hydrolysis of total extract (3), namely, 0.5 per cent.; on clarification of the concentrated liquor, however, the number (3) fell to 0.01 to 0.08 per cent. Similar results were obtained with quebracho.

Eitner and Procter showed that extraction under pressure caused loss of tannin in some cases, but this is not so great as some think; quebracho is little changed at 2 kg. pressure and difficult soluble tans go into solution. The loss with chestnut wood is practically zero; the lowering of tannin ratio is rather due to increased content of non-tans through hydrolysis of ordinarily insoluble substances, gums, pectins, fiber, etc., in presence of acids. The less acid in character the material, the less non-tans are formed, and the higher may be made the temperature of extraction. *Oak Wood Extract.*—The European factories are all in Slavonia, the crude material being the waste from parquet lumber. The trees growing on swampy land are richest in tannin, the reverse from chestnut. The wood of young oak is practically worthless for extraction, although the bark of young trees contains most tannin; this tannin is not the same, however, as that of the wood. Old wood contains 4 per cent. tannin. *Chestnut Wood Extract.*—This is worked mostly in Italy and France. The upland trees give the lightest colored extract and are not used under 60-70 years old. Trunk wood is the richest; roots are also rich, but contain a different tannin. The wood contains 7 to 9 per cent. of tannin. *Sumac.*—The best is the Sicilian (*Rhus coriaria*), being lightest colored and richest. Next come the varieties from Tuscany and Spain. The Tyrol sumac is from *Rhus cotinus*, the Swedish and Russian sumac from the bearberry, *Arbutus* (*Coriaria uva ursi*); French sumac is from *Coriaria myrtifolia*. The leaves are sold whole or powdered which last is often adulterated, principally with lentiscus leaves which contain 10-15 per cent. tannin. Guaranteed Sicilian sumac contains 20.2 to 26.5 per cent. Among other materials, mangrove is a useful tanstuff, combined with others such as quebracho and pine. The tannin content is: Madagascar 43-44 per cent., Celebes 45-48, E. Africa 38-42; the S. American mangrove is poorer. Another material, myrobalans, the dried fruit of an Indian tree, contains when of good grade, 38-40 per cent. tannin. By removing the seeds, the richer hulls bring up the ratio to 53.7 per cent. and are also exported in this form. Mimosa bark, from S. Africa and

Digitized by Google

Australia, 35.40 per cent. tannin, does not extract fully because of its fibrous character (this also applies to oak bark).

The technology of extraction is next described. Wood is first sliced transversely to the fiber in 3 mm. chips by feeding the logs against rapidly revolving cylinders faced with strong knives. To promote extraction the dust is blown out before delivery to the diffusors. These formerly consisted of open wooden vats, such as are still used for sumac extraction. Their advantage is in giving a richer and better colored extract, there being no decomposition by heating under pressure. But the yield, through imperfect leaching, is low and now closed extractors of copper are usually employed; 6 vessels serve for oak, chestnut, etc., while 10 to 12 are required for difficult soluble material, like quebracho. These diffusors sometimes reach 15 cu.m. capacity. The usual process is by boiling with direct steam, being rapid and giving concentracted liquors. The diffusion process is slower and gives thin liquors, but any decomposition of tannin is avoided. The concentrated liquors from extraction which have sp. gr. 1 to 2° Be with oak, progressing with chestnut and quebracho up to 12° with mangrove, are finally evaporated in vacuum apparatus to syrupy extracts of 20-30° Be or sometimes to solid form. The spent wood from the extraction is burnt and in chestnut extraction suffices for sole fuel. Special furnaces are used in which the moist residue (50-60 per cent. H_2O) is dried and then destructively distilled and finally burned. For spent quebracho, Böttger & Co. of Dresden furnish an efficient firing apparatus in which the material is first dried by flame as it slides down a grade, and is then burned beneath the boilers. The author is now obtaining good experimental results in applying his firing drum for coal dust (patent Aussig) to wet wood; the efficiency is 1.6 times that of the method first described.

Before evaporation, the extraction liquor is sometimes cooled for clarification, by circulating through pipes. Formerly this was accomplished by surface exposure to the air, but this caused darkening through oxidation and has been abandoned. It is important to exclude light and air during the entire manufacture. At 15° the insoluble sediment has separated sufficiently for ordinary demands. For chemical clarification, many agents are used; animal blood(patent Gondolo), lead nitrate, alum, sulphites, etc. These all produce precipitates and lighten the color of the extract. The reducing process by hydrosulphites (patent Badische Fabrik) bleaches without precipitation and the author has observed good results with these reagents (Blankit, Rongalit, Decrolin, Deflavit), but the process is expensive. Arnoldi's aluminum bleach is also too dear. The economically successful processes are those with sulphites (Lepetit and others) and that of Redlich (Triumph Extract). W. J. K.

Swelling in Sole Leather Tannage. W. Eitner. *Gerber,* 1912 [38], 57-8, 71-3, 86-8. Sole leather may be made solid after tannage by impregnation with fillers and excess of tannin or by hammering and rolling which processes serve for ordinary demands. For special purposes, for

Digitized by Google

example, army requirements, the leather must have a *natural* solidity or firmness and this depends upon the swelling. By merely softening a dried hide in water, the amount taken up is about 75 per cent. of that in the green hide. In the presence of alkalies or acids, this amount is increased and may even considerably exceed the natural amount, producing not only an increase in volume but a tension or becoming elastic ("prall") which is an external symptom only of the essential internal change. This consists of an intimate penetration of water within the fibers enveloping each particle. The great amount of surface hereby exposed for absorption of tannin explains the importance of the swelling operation. Its effect can be seen in a sour tannage. Rhenish oak sole leather gives no glue on boiling with water while sweet tanned leather swells, yielding glue, and further becomes transparent on soaking in 25 per cent. acetic acid which does not affect the Rhenish leather. The normal swelling, however, only ensues with acids; von Schröder showed that alkalies reduced the fixation of tannin, which had already been learned in practice. Hides swollen from the limes and entered direct in the vats never gave a full, solid leather. The acid was expended in neutralizing the alkali, the swelling fell and the lime salts themselves interfered with the action of the tannin.

Both kinds of swelling may be used properly directed. With many sorts of dried "wild" hides softening with sodium sulphide directly after dehairing and neutralization with sulphuric acid have proved useful. By this process dried up and even sunburnt ware can proceed with swelling and subsequent tannage like normal raw hides. Hides of old cattle which likewise do not plump well in the vat liquors can be made actually sensitive to these by first swelling in caustic alkali, then neutralizing and bringing into the sour vats in which they now plump well and tan thoroughly; any other method would fail.

Although it is possible to soften old hides in acid baths (as is recommended by acid manufacturers), this does not prepare directly for dehairing and a neutralization or lengthy watering must intervene. The alkaline soak prepares directly for liming. As far as softening of the fiber is concerned, the result of alkaline swelling is permanent, even after neutralizing. In acid swelling, which is proper to the tanning process, the effect ceases when the acid is removed and also requires a certain length of time, being gradual. It is not practical to tan in the drum sole leather requiring an intense acid swelling. For drum tannage, an alkaline swelling was early found to be also unsuited. In swelling for drum tannage, a fore-tannage of at least 12 vats should be carried out at the same time. By employing also a system of "Versenks," the necessary acid may be furnished by the tan liquors in the case of vache leather. For heavy sole leather the swelling may also be effected successively in the vats with sour liquors, or quickly in separate swelling vats with artificial acids. Large amounts of acid liquor are furnisehd by

Digitized by Google

the pine bark used in the "Versenks," but it is generally necessary to strengthen with an organic acid such as formic acid.

If one wishes heavy coarse leather of high weight, a separate swelling bath of sulphuric, hydrochloric or oxalic acid may be used. The swelling thus produced disappears on tanning in sweet liquors as the acid diffuses out. The recent statement of a professor of the tanning art that the acid must be washed out of hides thus plumped before entering tan liquors is ridiculed. On the contrary the acid must remain in the hide and the liquor itself be acid, else the swelling falls and its effect is lost. The author's suggestion to fix the mineral acid swelling by a formaldehyde bath has proved practical for heavy leather although without benefit for vache leather. Formaldehyde has often been misused however; when applied before swelling, this is retarded, and put in the vats it precipitates tannin or is otherwise made ineffectual. This formaldehyde "hardening" can be used with advantage when the hides are inclined to shrink in the liquors, also when the initial tannage is carried out with strong liquors containing cheap materials like knoppern, divi-divi, myrobalans, etc. The hardening bath contains 1 kilo formaldehyde to 10 hectoliters water, in which the hides hang 24 hours. The bath may be often used, strengthening with one-half the original amount.

In general, hide should not be plumped, especially in a special bath, before giving the grain a fore-tannage in sweet liquor to prevent its swelling. If the grain be swollen first it will be brittle. Swelling can sometimes proceed abnormally; overswelling is not likely to ensue with sulphuric acid which does not swell beyond a certain strength. Hydrochloric acid is less certain and organic acids are the most difficult to control, most of all laevo-lactic acid (rare), then butyric acid, next acetic acid, ordinary lactic acid, formic acid. Falling back of swelling occurs oftener than over-swelling. The cause is leaching out of the acid into weak liquors containing little acid or fermentation changes in the liquors.

W. J. K.

PATENTS.

Process of Unhairing Hides and Skins. U. S. Patent No. 1,019,854. LOUIS STERN, Newark, N. J.

Liquid air is applied to the roots of the hair, which thus is made very brittle, and may be rubbed off.

Sewage Separator. U. S. Patent No. 1,019,907. JAMES S. MILLER, Reading, Pa.

Treatment of Sewage. U. S. Patent No. 1,019,933. JOE SMITH WADDINGTON, Bradford, England. Machine for extracting liquid from sewage.

Composition of Matter. U. S. Patent No. 1,020,497.

Treatment of Rawhide. U. S. Patent No. 1,020,498.

Digitized by Google

Fabric or Cloth. U. S. Patent No. 1,020,499.

These three related patents have been granted to Albert H. Henderson, Baltimore, Md., assignor to the Henderson Rubber Company, Baltimore. The first and second involve a process of treating fragments of rawhide with oil, which swells it, and then dissolving out the oil, the rawhide being thus left swollen. The hide is then penetrated with a solution of rubber. The third patent relates to fabrics from which oil, etc., have been removed by mercerization. These are filled in with rubber which is afterward vulcanized.

Process of Making a Composition of Matter for the Treatment of Leather, Fabrics and the like. U. S. Patents Nos. 1,020,926 and 1,020,927. DANIEL O'KEEFE, St. Louis, Mo.

The material is a mixture of fish oil, turpentine, petroleum, bay oil, cedar oil, mirbane oil and mustard oil.

Machine for Brushing and Cleaning Leather. U. S. Patent No. 1,021,007. WILLIAM R. SMITH, Buffalo, N. Y.

Glove Leather and Process of Preparing It. U. S. Patent No. 1,021,380. EDMUND SIMON, Dresden, Germany.

The process includes tawing the skins and treating them with a liquor containing salicylic acid ester and benzoic acid ester. The claim is made that glove leathers often contain traces of the foul materials used in manufacture, causing the leather to mold, and endangering the hands of the wearer. The new leather is said to be antiseptic.

Evaporating Apparatus having Multiple Evaporation. U. S. Patent No. 1,021,486. WACLAW RUSIECKI, Rakitnaja, Russia.

Manufacture of Volatile Organic Acids from Their Calcium Salts. U. S. Patent No. 1,023,281. RALPH S. SWINTON, Linden, N. J., assignor to W. J. Bush & Co., Dover Del. The dry, granular calcium salt is subjected to the progressive action of sulphuric action slowly introduced at the bottom of the vessel.

Process of Making Anhydrous Sulphites and Bisulphites. U. S. Patent No. 1,023,179. E. H. STRICKLER, White Plains, N. Y., assignor to the General Chemical Co., N. Y. Sulphur dioxide and carbonate of soda are brought together in a solution of a sodium salt, the sodium carbonate being in the form of a suspended solid.

Process for the Preparation of Chrome Leather. U. S. Patent No. 1,023,451. ALBERT WOLFF, Cologne, Germany. The patent covers the ues of chromium formate in one-bath chrome tannage.

Machine for Stretching Hides and Skins. English Patent No. 25,990. E. SIMEON, Grenoble, France.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII JUNE, 1912 No. 6

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, } . . . . . Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

CHANGES OF ADDRESS.

Albert L. Burwell to Huntington Park, Los Angeles, Cal.

G. G. Eysenbach to 310 Jackson Ave., Ridgway, Pa.

LETTER TO THE EDITOR.

EDITOR A. L. C. A. JOURNAL:

The steady growth of the American Leather Chemists Association must be a matter of pride to the Leather Chemists who organized the A. L. C. A. a comparatively few years ago. With no pecuniary advantage accruing to the officers and directors, either direct or indirect, still the work of the Association has been carried on as a labor of love and its influence each year has

Digitized by Google

widened as its growth has extended. As an associate member, I think I voice the general feeling of the associate members that all commendation and credit for the American Leather Chemists Association belong to the active members who organized and have so successfully maintained the Association from its beginning to the present.

In spite of this success, I frequently hear the active members wish for a larger degree of usefulness and especially for more coöperation on the part of the associate members in the work of the Association. In view of the results already obtained it might seem unwise to suggest any change in management or organization, but growth involves change and it may be that the plan of management in the early days of the A. L. C. A. may now wisely be changed. I venture to suggest that this more active coöperation would be furthered if the voting rules were changed so as to permit the associate members to vote for officers and participate with the chemists in the management of the Association.

It is universal experience, that interest in an organization is increased where the personal element enters through an opportunity to vote. I have observed this to be the case, whether the organization is a Sabbath School class of young boys or whether it is a group of a thousand American business men engaged in the organization of a National Association of Commerce. The meeting gets busy and interest increases when an election of officers occurs. It is the natural American instinct.

The tanners or the extract manufacturers or any of the other associate members of the A. L. C. A. have no desire to control the management of the A. L. C. A. Indeed, I think these gentlemen are quite willing to leave this burden on the shoulders of the chemists, but I do believe that these men who are now associate members would be more apt to be drawn into closer coöperation with the chemists if they were compelled by the voting privilege to share with the chemist in the actual responsibility of the management of the Association.

The objection may be raised that this would tend to make the organization more of a commercial body and less of a scientific body. In reply to this, it can be said that certain commercial elements have to-day virtually a representative in the active

Digitized by Google

membership of the Association through employees and officers who are active members, these companies having an advantage, if there be any advantage in active membership, over their friends and competitors who do not happen to have chemists associated with them.

This is a suggestion. I would like to see the matter discussed in the JOURNAL.

AN ASSOCIATE MEMBER.

REPORT OF THE COMMITTEE APPOINTED TO REVISE THE WORDING OF THE OFFICIAL METHOD FOR TANNIN ANALYSIS.

The Committee in considering the subject has decided that any revision of the Official Method that confined itself strictly to alterations in the wording without change in procedure would be of practically little value and in many instances impracticable. Therefore the result of their deliberations is in the form of a revised method in its true sense, and includes the results of much work done for the Association, both by individual members and committees, which has not received the recognition that in the opinion of the Committee it deserves.

In submitting the report the Committee feels that it should to the best of its ability endeavor to explain the why and the wherefor of the various suggested alterations in the method even though to many of the members of the Association the reasons are perfectly apparent. Each paragraph of the suggested revised method is therefore considered separately in the ensuing explanatory comments.

I. RAW AND SPENT MATERIALS.

(1) *Caution*:

It is apparent that this change, in conjunction with (2, b), prevents the reporting of analyses of new materials with a less water content than they contain, to a greater degree than does the present Official Method.

(2) *Preparation of Sample*:

No material alteration from the present method is made by this paragraph other than the one commented upon under (1).

Digitized by Google

(3) *Water Determination*:

No change in method instituted.

(4) *Amount of Sample to be Extracted*:

The present method calls for a dilution for analyses containing between 0.35 and 0.45 gram tannin per 100 cc. The Committee believes that it is perfectly practicable to narrow the limits to between 0.375 and 0.425 gram tannin per 100 cc. without imposing unnecessary hardship upon the analyst, while bringing the strength of the analysis solutions in greater uniformity. This, in conjunction with the narrowing of the limits of the actual dry hide powder used in detannizing, and the narrowing of the limits of the water content of the wet hide (see 12, a), should effect greater concordance in the non-tannin determination, since the amount of hide to tannin must of necessity be in better concordance in various laboratories, and the fact is well established that the greater the proportion of hide to tannin the less non-tannin returned. Again, the effect upon the insolubles will be in the line of better uniformity more particularly in the analysis of those materials containing high insolubles, it being equally well established that the wider the variation in the strength of the analysis solution the wider the variation in the resulting insolubles.

(5) *Extraction*:

The Committee has endeavored to be as explicit as possible in defining the character of the extracting apparatus to be employed in the belief that uniformity in analysis will result only by rigid adherence to the details of extraction. In line with this is the method (A) "Woods, Barks and Spent Materials," where the time and applied heat are specifically stated and the gelatine-salt test for the completion of extraction as given in the Official Method eliminated, as sufficient evidence has been presented to show the lack of conclusiveness of the test (JOURN. A. L. C. A., Vol. II, pgs. 275-279). (B) "Materials other than Woods, Barks and Spents," does not change the present method other than in specifying exactly 7 hours for extraction instead of from 6 to 8 hours. The Committee has added a clause to the effect that the material of the boiling flask must be inert to the percolate. It has been shown that copper flasks have a decidedly detrimental

Digitized by Google

effect upon tannin solutions upon continued boiling (JOURN. A. L. C. A. Vol. II, pg. 274). It has been suggested that tinned copper may not have the destructive action upon tannin solutions shown by copper. The Committee suggests that experiments be undertaken to prove the point.

In addition the references already quoted the following have strengthened the Committee in arriving at the conclusion to make alterations in the method in the particulars cited under (5).

"An Extractor for Tanning Materials." Reed, Vol. I, pg. 176 et seq., pg. 183 et seq.

"Extractors for Tanning Materials." Teas, Vol. I, pg. 274 et seq.

"An Improved form of Soxhlet for Tannin Extraction." Delaney, Vol. V, pg. 348 et seq.

"Extraction of Tanning Materials." Committee Report 1907; Vol. II, pgs. 279-280.

"Extraction of Sumac and Myrobalans." Eachus, Vol. III, pgs. 297-301.

(6) *Analysis*:

The change in this paragraph from the present method is in the elimination of the allowability of reducing the amount of hide powder in the case of weaker dilutions than the Official Method specifies. This applies practically altogether to the analysis of spent materials, and the Committee would give the following reference as sustainng the point in question:—

"Non-Tannins in Solutions of Different Density with Varying Amounts of Hide Powder." Alsop, JOURN. A. L. C. A., Vol. II, pg. 403.

II. ANALYSIS OF EXTRACTS.

(7) *Amount and Dilution for Analysis*:

(A) *Fluid Extracts*:

The amount of sample taken for analysis has already been commented upon.

The method suggested for dissolving by washing into the flask with 900 cc. water at 85° C. is in the opinion of the Committee much superior to the present method.

Digitized by Google

(a) The permission given by the proposed method to rapidly cool analysis solutions is, the Committee feels, warranted by work that the Association has done, and, in conjunction with a rapid-chroming method (see 12, b) serves to curtail the time required for analysis by a day. The following references are cited to confirm the conclusion of the Committee to advocate a rapid-cooling method:

Committee on Soluble Solids.

Wilson, JOURN. A. L. C. A., Table, Vol. I, pgs. 13-15.
Eachus, JOURN. A. L. C. A., Vol. IV, pgs. 310-322.
Maxwell, JOURN. A. L. C. A., Vol. V, pgs. 510-526.

Particular attention is called to the reference Vol. V. The results there shown by seven collaborators on an ordinary quebracho extract are markedly in favor of the rapid-cooling method in point of concordance of results between analysts. The Official Method gives a maximum insoluble difference of 1.91 per cent., Method II (cooled under tap) a maximum difference of 1.26 per cent. and Method III (cooled with water at 15° C.) a maximum difference of only 0.69 per cent. As there can be no question but that the colder the water used for cooling solutions the greater the liability of precipitation, it follows that the more closely the temperature of the cooling medium approaches the temperature to which it is desired to bring the solutions for analysis the less chance of precipitation. In other words, it is safer to use water at a temperature of 19° C. for cooling than water at 15° C. even though the latter in the reference alluded to gave markedly better concordance than did the present method.

(b) The Committee feels that by permitting the present method to stand in so far as allowing the solutions to stand over night before analyzing the versatility of the method will be increased, as samples received too late in the day for analysis may be dissolved and be ready for analysis in the morning thereby effecting a considerable saving in time.

(B) The method of dissolving solid extracts is unquestionably a distinct improvement upon the Official Method. It is a method which can be followed to the letter and leave no room for discussion as to correct procedure.

Our method now, strictly interpreted, does not allow the use

Digitized by Google

of two liter solution. It would seem a wise provision to permit this and especially in the weighing out of certain solid and powdered extracts is accuracy fostered by the double quantity of sample taken.

(8) *Total Solids*:

No change has been made in this paragraph.

(9) *Water*:

Our present method contains no clause providing for water determination.

(10) *Soluble Solids*:

An omission in the present method is in any specification as to the quality of the kaolin used. This has been rectified in the proposed method.

Instead of stirring the kaolin with 75 cc. of solution the Committee recommends sufficient solution to fill the paper.

The really important alteration in this item of the analysis has to do with temperature regulations, and although it is fully understood that these changes may impose a burden upon the analyst yet the Committee, realizing the importance that absolute uniformity in procedure has upon the ultimate result in respect to concordance, urges the changes they recommend to the most careful consideration of the Association. The method of cooling has already been described under (7). The temperature of the solution on the paper must not fall below 20° C. nor rise above 25° C. The reason for such prescription is obvious to all chemists performing tannin analyses. In the summer months when the temperature of the laboratory is high there is no question but that the insolubles are less than during the cooler months when it is possible to keep the temperature, approximately at any rate, at 20° C. The ability to keep the temperature below 25° C. in warm weather is aided by the fact that the proposed method specifies that the temperature of the solution in the flask must be kept at 20° C. The Committee considered the alternative of specifying that the temperature of solutions be kept uniformly at 20° C. throughout filtration, which would necessitate jacketing funnels for cold water circulation or some similar device, but considered that so radical a change would be hardly wise

Digitized by Google

calling as it would for no inconsiderable additions to laboratory fittings.

(11) *Insolubles*:

It seems strange that our present method provided not at all for the item of insolubles.

(12) *Non-Tannins*:

Hitherto our method has required no standard for hide powder. It was thought wise to have this written into the method particularly as to the acidity of the powder. In deciding upon the proper range of acidity the Committee consulted the following references:

Small, JOURN. A. L. C. A., Vol. II, pgs. 347-355.
Reed, JOURN. A. L. C. A., Vol. II, pgs. 435-438.
Reed, JOURN. A. L. C. A., Vol. III, pgs. 333-334.
Eachus, JOURN. A. L. C. A., Vol. IV, pgs. 310-322.
Tucker, JOURN. A. L. C. A., Vol. IV, pg. 325.

(a) That the amount of water to hide might be uniform the Committee has recommended that the chrome alum be in 3 per cent. solution. Our present method is lax in its specifications for washing the chromed hide powder. As it is practically impossible to wash until the wash water gives no test for sulphates with barium chloride, and as it is undeniably true that too much washing has the effect of getting the powder in a condition in which it will not detannize properly, it was thought best to specify exactly the amount of water, time and manner of washing, thus bringing all laboratories into accord and therefore making toward uniformity. Distilled water is also called for by the revision and the present method is greatly at fault in not requiring it for washing the powder. The wet hide powder used for the analysis at present must contain from 70 to 75 per cent. water. The proposed method narrows these limits to from 71 to 74 per cent. With the same end in view, that of better concordance, the Committee have advised that the limits of the dry hide be not less than 12.2 nor more than 12.8 grams to 200 cc. of the solution instead of 12 to 13 grams as at present. The word "immediately" has been added in order that time might not elapse between adding the solution to the wet hide

Digitized by Google

and the shaking operation. As flasks graduated to deliver 200 cc. are recommended for measuring the solution to be detannized there is nothing to prevent the "immediate" shaking. The paper for filtering the non-tannin solutions is specified as "single" in the proposed method.

(*b*) An important change in the revision recommended by the Committee is in permitting a rapid chroming method. Reference to work that has been done on rapid chroming in comparison with over-night chroming shows that the two methods are very comparable when the former is rightly conducted. The Committee consulted the references below:

Report 1908 Committee, JOURN. A. L. C. A., Vol. III, pg. 330.

Report 1909 Committee, JOURN. A. L. C. A., Vol. IV, pgs. 310-322.

Report 1910 Committee, JOURN. A. L. C. A., Vol. V, pg. 419-426.

The gelatine-salt test for the presence of tannin in the non-tannin filtrate has been eliminated. There has always been a question as to what course to pursue when a non-tannin filtrate of a tannin solution made up officially gave a test for tannin with gelatine-salt solution. It seemed to the Committee that the amount of hide powder used to detannize was sufficient to effect complete detannization with all solutions of official strength when the tanning material was of proper character. Also it has been proved that the gelatine-salt test is of doubtful reliability.

(13) *Tannin*:

The phrase "and represents the matters absorbable by hide under the conditions of the prescribed methods" is an addition to the present method which the Committee feels is a wise one and which needs no elucidation.

III. ANALYSIS OF LIQUORS.

(14) *Dilution*:

The addition to this clause of the present method is evidently a proper one as liquors that will not dissolve readily in cold water are sometimes met with.

Digitized by Google

(15), (16), (17), (18).

These show practically no change from the present Official Method.

(19) *Temperature*:

This is an added clause and one the Committee believes should meet the approval of the Association.

The Committee suggests no further change in the method in paragraphs (20) and (21) nor in the determination of the total acidity of liquors.

The Committee submits this report to the Association trusting that it will have the most careful and conscientious consideration from all its members, and firmly believing that the adoption of the revised method proposed will be a distinct step in advance, conducing to greater concordance in analysis and therefore to greater confidence in the Association, its members and its methods.

H. C. REED, Chairman,
F. H. SMALL,
J. H. YOCUM.

PROPOSED OFFICIAL METHOD OF THE AMERICAN LEATHER CHEMISTS ASSOCIATION FOR THE ANALYSIS OF VEGETABLE MATERIALS CONTAINING TANNIN.

I. RAW AND SPENT MATERIALS.

(1) *Caution*:

Proper care must be taken to prevent any change in the water content of raw materials during the sampling and preliminary operations. (See "General" under Sampling.)

(2) *Preparation of Sample*:

The sample must be ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

(a) The temperature used for drying samples of spent material for grinding must not exceed 60° C.

(b) Samples of raw material too wet to be ground may be dried before grinding as in (a). In this case a preliminary

Digitized by Google

water determination must be made according to (IV) on the sample as received. If the portion of the sample taken for the water determination is in pieces too large to dry properly, it is permissible to reduce these to smaller size as rapidly and with as little loss of water as possible.

(3) *Water Determination*:

Ten grams of the ground material shall be dried in the manner and for the period specified for evaporation and drying in extract analysis (see IV).

(4) *Amount of Sample to be Extracted*:

Such an amount of raw material shall be extracted as will give a solution containing as nearly as practicable 0.4 gram tannin to 100 cc. (not less than 0.375 or more than 0.425). Of spent materials such an amount shall be taken as will give a solution of as nearly as practicable the above concentration.

(5) *Extraction*:

Extraction shall be conducted in an apparatus consisting of a vessel in which water may be boiled and a container for the material to be extracted. This container shall be provided above with a condensation chamber so arranged that the water formed from the condensed steam will drip on the material to be extracted, and provided below with an arrangement of outlets such that the percolate may either be removed from the apparatus or be delivered to the boiling vessel. The boiling vessel must be so connected that it will deliver steam to the condensation chamber and that it may receive the percolate from the container. The condensation water from the condenser must be at approximately the boiling temperature when it comes in contact with the material to be extracted.

The material of which the boiling flask is composed must be inert to the extractive solution. Suitable provision must be made for preventing any of the solid particles of the material from passing into the percolate.

(A) *Woods, Barks and Spent Materials*:

Five hundred cc. of the percolate shall be collected outside in approximately two hours and the extraction continued with 500 cc. for 14 hours longer by the process of continuous extrac-

Digitized by Google

tion with reflux condenser. The applied heat shall be such as to give by condensation approximately 500 cc. in 1½ hours.

(B) *Materials Other than Woods, Barks and Spent*:

Digest the material in the extractor for one hour with water at room temperature and then extract by collecting two liters of percolate outside in approximately 7 hours.

(6) *Analysis*:

The percolate shall be heated to 80° C., be cooled, made to the mark and analyzed according to the official method for extracts.

II. ANALYSIS OF EXTRACTS.

(7) *Amount and Dilution for Analysis*:

(A) *Fluid Extracts*:

Fluid extracts shall be allowed to come to room temperature, be thoroughly mixed, and such quantity weighed for analysis as will give a solution containing as nearly as possible 0.4 gram tannin to 100 cc. (not less than 0.375 nor more than 0.425). Precautions must be taken to prevent loss of moisture during weighing. Dissolve the extract by washing it into a liter flask with 900 cc. of distilled water at 85° C.

Cooling:

(a) The solutions prepared as above shall be cooled rapidly to 20° C. with water at a temperature of not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with at once, or

(b) The solution shall be allowed to stand over night, the temperature of the solution not being permitted to go below 20° C., be brought to 20° C. with water at not less than 19° C., be made to the mark with water at 20° C. and the analysis proceeded with.

(B) *Solid and Powdered Extracts*:

Such an amount of solid or powdered extract as will give a solution of the strength called for under liquid extracts shall be weighed in a beaker with proper precautions to prevent change of moisture. One hundred cc. of distilled water at 85° C. shall be added to the extract and the mixture placed on the water-bath, heated and stirred until a homogeneous solution is obtained.

Digitized by Google

When dissolved, the solution shall immediately be washed into a liter flask with 800 cc. of distilled water at 85° C., be cooled, etc., as under (A) above.

Note: It is permissible to make up 2 liter instead of 1 liter solutions, dissolving by washing into flask with 1,800 cc. water at 85° C. in case of fluid extracts and 1,700 cc. water at 85° C. in case of solid or powdered extracts.

(8) *Total Solids*:

Thoroughly mix the solutions; pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying." (See IV.)

(9) *Water*:

The water content is shown by the difference between 100 per cent. and the total solids.

(10) *Soluble Solids*:

S. & S. No. 590, 15 cm. single, pleated, filter paper shall be used for the filtration.

The kaolin used shall answer the following test: 2 grams kaolin digested with 200 cc. of distilled water at 20° C. for 1 hour shall not give more than 1 mg. of soluble solids per 100 cc., and shall be neutral to phenolphthalein. To 1 gram kaolin in a beaker add sufficient solution to fill the paper, stir and pour on paper. Return filtrate to paper when approximately 25 cc. has collected, repeating operation for 1 hour, being careful to transfer all kaolin to the paper. At the end of the hour remove solution from filter paper, disturbing the kaolin as little as possible. Bring so much as needed of the original solution to exactly 20° C. as described under (7), refill the paper with this solution and begin to collect the filtrate for evaporating and drying so soon as it comes CLEAR. The paper must be kept full and the temperature of the solution on the filter must not fall below 20° C. nor rise above 25° C. during this part of the filtration. The temperature of the solution used for refilling the paper must be kept uniformly at 20° C. and the funnels and receiving vessels must be kept covered.

Pipette 100 cc. of clear filtrate into tared dish; evaporate and dry as under (8).

Digitized by Google

(11) *Insolubles*:

The insoluble content is shown by the difference between the total solids and the soluble solids, and represents the matters insoluble in a solution of the concentration used under the temperature conditions prescribed.

(12) *Non-Tannins*:

The hide powder used for the non-tannin determination shall be of woolly texture, well delimed, and shall require between 12 and 13 cc. of N/10 NaOH to neutralize 10 grams of the absolutely dry powder.

(a) Digest the hide powder with 10 times its weight of distilled water till thoroughly soaked. Add 3 per cent. of chrome alum ($Cr_2SO_4)_3K_2SO_4 24H_2O$, in 3 per cent. solution) calculated on the weight of the air-dry powder. Agitate frequently for several hours and let stand over night. Squeeze and wash by digesting with 4 successive portions of distilled water, each portion equal in amount to 15 times the weight of the air-dry powder taken. Each digestion shall last for 15 minutes, and the hide powder shall be squeezed to approximately 75 per cent. water after each digestion except the last, a press being used if necessary. The wet hide powder used for the analysis shall contain as nearly as possible 73 per cent. of water, not less than 71 per cent. nor more than 74 per cent. Determine the moisture in the wet hide powder by drying approximately 20 grams. (See IV.) To such quantity of the wet hide as represents as closely as practicable 12½ grams (not less than 12.2 nor more than 12.8) of absolutely dry hide add 200 cc. of the original analysis solution and shake immediately for 10 minutes in some form of mechanical shaker. Squeeze immediately through linen, add 2 grams of kaolin (answering test described under (9)) to the detannized solution and filter through single folded filter (No. 1F Swedish recommended) of size sufficient to hold the entire filtrate, returning until clear. Pipette 100 cc. of filtrate into tared dish, evaporate and dry as in (8).

The weight of the non-tannin residue must be corrected for the dilution caused by the water contained in the wet hide powder.

Digitized by Google

Funnels and receiving vessels must be kept covered during filtration. Flasks graduated to deliver 200 cc. are recommended for measuring the analysis solution to be detannized.

(b) Digest the hide powder with the amount of water and add the amount of chrome alum in solution directed under (a).

Agitate in some form of mechanical shaker for 1 hour and proceed immediately with washing and subsequent operations as directed under (a).

Note: In order to limit the amount of dried hide powder used, determine the moisture in the air-dry powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing as nearly as possible 73 per cent. of water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

(13) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannins, and represents the matters absorbable by hide under the conditions of the prescribed methods.

III. ANALYSIS OF LIQUORS.

(14) *Dilution*:

Liquors shall be diluted for analysis with water at room temperature so as to give as nearly as possible 0.7 gram solids per 100 cc. of olution. Should a liquor be of such character as not to give a proper solution with water of room temperature it is permissible to dilute with water at 80° C. and cool rapidly as described under (7, A, a).

(15) *Total Solids*:

To be determined as in Extract Analysis.

(16) *Soluble Solids*:

To be determined as in Extract Analysis.

(17) *Insolubles*:

Determined as in Extract Analysis.

Digitized by Google

(18) *Non-Tannins*:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing as nearly as possible 73 per cent. water, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry powder per 200 cc.
0.35 —— 0.45 grms.	9 —— 11 grms.
0.25 —— 0.35 grms.	6.5 —— 9 grms.
0.15 —— 0.25 grms.	4 ——6.5 grms.
0.00 —— 0.15 grms.	0 —— 4 grms.

Solutions to be shaken for non-tannins as in Extract Analysis and 100 cc. evaporated as in Extract Analysis.

IV. TEMPERATURE, EVAPORATION AND DRYING, DISHES.

(19) *Temperature*:

The temperature of the several portions of each solution pipetted for evaporating and drying, that is, the total solids, soluble solids and non-tannins must be identical at the time of pipetting.

(20) *Evaporation*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer" at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

(21) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor more than 3 inches in diameter.

V. DETERMINATION OF TOTAL ACIDITY OF LIQUORS.

Note: No change in method.

Digitized by Google

APPLICATIONS OF THE LAW OF MASS ACTION TO SOME OF THE REACTIONS OF THE TANNING PROCESS*

By Edmund Stiasny.

A complete understanding of the reactions involved in tanning is in many cases possible only on the basis of physico-chemical laws. The study of the plumping and falling phenomena and the colloid-chemical behavior of the hide-proteins and of the tannins are examples of the more complex of these problems, the great difficulties of which can only be solved very gradually. There are, however, some simpler processes, the explanation of which can be given by applying the mass rule, which at the same time enables valuable conclusions to be drawn. The deliming of limed hides and the neutralization of chrome leather are processes of this kind and may be discussed in the following pages.

I. DELIMING OF HIDES.

Limed hides after mechanical unhairing and fleshing are washed several times with water, though thereby only a part of the lime can be removed. The thorough deliming is done by means of acids and often completed by bates. As a rule when deliming with acid it is necessary to remove from 0.4 to 1 per cent. CaO (per cent. of the pelt weight). This deliming requires much attention, as an excess of acid must be carefully avoided so as not to produce an acid plumping. The danger of an excess of acid is the greater, the stronger the acid is, and therefore most tanners prefer the weak organic acids (lactic acid, acetic acid, formic acid and more recently butyric acid) to the strong inorganic acids (hydrochloric acid). The most favorable action would in all probability be obtained by an acid which is so weak that it has no swelling effect at all, and therefore could be used in excess. H. R. Procter has shown in his valuable work on acid swelling, that the limit of swelling power lies at a concentration of the actual hydrions of $C_h = 10^{-5}$ to 10^{-4}. This important discovery forms the basis of the following deliberations. An acid which when diluted for use, shows a lower hydrion concentration than 5.10^{-5} and which is present in sufficient quantity for complete deliming, will not do any harm if used in excess

Read at the Washington convention of the A. L. C. A., Dec., 1911.

Digitized by Google

and will produce an absolutely lime-free hide. Assuming that the deliming is done in the paddle with a quantity of solution four or five times the pelt weight, and that the amount of lime present in the hide amounts to 0.6 per cent. CaO, then this would call for the use of about a $^1/_{20}$N acid, for

$$\frac{600}{28 \times 400} = 0.054.$$

The strength of an acid is given by its dissociation constant. Therefore the magnitude of the dissociation constant must first be determined for any acid which in $^1/_{20}$N-solution has a hydrion concentration of about 10^{-5}. According to the mass rule we have $K.C_{HX} = C_{\dot{H}} . C_X, = C^2_{\dot{H}}$, in which K is the dissociation constant, C_{HX} the concentration of the undissociated acid molecules and $C_{\dot{H}}$ the hydrion concentration. As $C_{\dot{H}} = 10^{-5}$, and C_{HX} for a very weak $^1/_{20}$N-acid is about 0.05, so we have for an acid which should show the above action,

$$K = \frac{C^2_{\dot{H}}}{C_{HX}} = \frac{10^{-10}}{0.05} = 2.10^{-9}.$$

Any acid, which shows a somewhat low dissociation constant, can be used for deliming purposes, if it fulfills the following conditions: It must form a soluble lime salt; it must be non-poisonous, odorless and low in cost. The only acid which fulfills these conditions and at the same time has a dissociation constant of 10^{-10} to 10^{-8} is boric acid. But the choice of acids can be much increased, as it is possible to produce a deliming solution having the desired properties, by mixing the solution of a suitable acid whose dissociation constant lies between 10^{-5} and 10^{-4}, with an equivalent amount of one of its soluble salts. Thereby the hydrion concentration is reduced below that necessary to produce a plumping action. According to the mass rule we have the equation $K . C_{HX} = C_{\dot{H}} . C_{X'}$, and from that $C_{\dot{H}} = \frac{K. C_{HX}}{C_{X'}}$ in which K, C_{HX} and $C_{\dot{H}}$ have the above mentioned meaning and $C_{X'}$ represents the concentration of the acid radical-ions. As the C_{HX} of a weak $^1/_{20}$N-acid is about 0.05 and $C_{X'}$ of a $^1/_{20}$N-salt solution is also about 0.05, we get $C_{\dot{H}} = K$. In other words, the

Digitized by Google

hydrion concentration of an equivalent mixture of a weak acid and its salt is equal to the dissociation constant of the acid.[1]

Therefore, for deliming purposes, any harmless, cheap acid can be taken which forms soluble lime salts and whose dissociation constant is not materially above 10^{-5}, and this acid must then be mixed with the equivalent amount of one of its salts or half of the acid can be neutralized, in order to obtain a deliming solution answering all conditions.

Such a solution is neutral to methyl orange and gives when titrated with phenolphthalein the amount of potential hydrions for deliming. These principles can be applied in practice by placing in a paddle, per 100 kilograms of the white weight, 1.28 kilograms acetic acid and 1.76 kilograms sodium acetate with 400 liters of water[2] and paddling the hides in this solution until a cross-section shows no lime (no reddening with phenolphthalein). For the stated amounts, the percentage of lime in the wet pelt is assumed as 0.6 per cent. The used bath can be brought back with little expense to its original state if sufficient oxalic acid is added to precipitate the dissolved lime.[3] This is carried out in a vat and the precipitated lime allowed to settle out, after which the supernatant solution containing the original proportion of acid to salt, is returned to the paddle. It is only necessary to add enough of the fresh acid and salt solution to replace the unavoidable loss in the operation. An excess of oxalic acid must be avoided and the deliming solution should always be neutral to methyl orange.

Instead of acetic acid and sodium acetate, butyric acid and sodium butyrate may be used. With this material it would be more economical to prepare the butyrate by neutralization of the butyric acid. The solution is prepared by dissolving 3 kilograms of crystallized soda in hot water and adding (while stirring) to the hot and somewhat concentrated solution 3.76 kilograms of butyric acid, continuing stirring until the carbonic

[1] See Ostwald : Grundriss der allgemeinen Chemie 1909, p. 461.

[2] For 100 lbs. hide, 1 lb. 4 ozs. acetic acid, 1 lb., 12 ozs. sodium acetate, 40 gallons water.

[3] The application of oxalic acid for liberating organic acids combined with lime was first proposed and applied by H. R. Procter for the purification of handler liquors.

Digitized by Google

acid gas has escaped.[4] The mixture of butyric acid and sodium butyrate is then placed in the paddle.

Instead of the soda salt, an ammonium salt may be prepared which would produce a preliminary bating. A mixture of butyric acid (or any other organic acid) and its salt may also be prepared by gradually deliming a pack of limed skins with successive small portions of butyric acid, adding the portions of acid when the solution reacts alkaline to phenolphthalein. The last portion of the acid, even after complete neutralization, will not produce any plumping effect, as considerable amounts of the soluble lime salt formed at first repress the dissociation of this excess of acid. The bath for the next pack is prepared by running off one-fourth of the used bath and adding as much acid as was used up for neutralizing the last pack, together with the necessary amount of water to fill the paddle. In continuous working it will be useful to control the deliming capacity of the liquor before a new pack is entered, by making a titration with phenolphthalein as indicator. This deliming capacity has to be kept constant, and the necessary amount of acid to do so will soon be found out in practice.

By this working system the amount of calcium butyrate which will be present in the bath after repeated use will be four times the salt produced by deliming one pack. Or if $\frac{1}{n}$ be the portion of the paddle liquor removed after each pack, the amount of calcium butyrate present will finally rise to n times the amount which is produced by deliming one pack. Hence the hydrion concentration of such a bath will come down to $C_{\dot{H}} = \frac{K}{n}$, where K is the dissociation constant of the acid.

As the hides or skins are slightly acid after this treatment and the bate which possibly follows requires a weak alkaline solution, it is advisable to agitate them for a short time in the paddle,

[4] Should carbonic acid remain dissolved in the water, it would combine with the lime of the hide to insoluble calcium carbonate which is not soluble in the deliming mixture and which would cause defects in the finished leather.

Digitized by Google

adding 1 per cent. of magnesium carbonate (on the pelt weight)[5] to the old bate, which can be used as a clearing bath.

Hides treated in this manner are well prepared for the bating which follows. For sole leather, a deliming of the outside portions will be sufficient, leaving the inner portions slightly alkaline, so that in this case the treatment with magnesium carbonate may be dispensed with.

2. NEUTRALIZATION OF CHROME LEATHER.

Chrome leather after thoroughly washing with water is treated with a neutralizing agent in order to remove any free acid present. In this neutralization, it is essential that no free acid remain, and also that no excess of alkali be used, for over-neutralization injuriously effects the appearance and compactness of the finished leather. It may be due to the alkali having a detrimental action on the leather fiber or it may be that the basic chrome salts are converted into chromium hydroxide, which is not to be desired. Therefore, we have, when neutralizing chrome leather, a case similar to the deliming of hides, requiring carefully regulated neutralization.

The question then arises, can we also determine here the limit of the hydroxyl-ion concentration, below which a weak alkali, even in excess will not exert a detrimental action? Such a limit, after many experiments, seems to lie at a hydroxyl-ion concentration of about 10^{-5}. If an alkali is selected which in 1/10 N solution (the usual neutralizing solutions are about 1/10 N) has no higher hydroxyl-ion concentration and is cheap, harmless, odorless and forms soluble sulphates and chlorides, then this substance may be used in excess without fear of getting bad secondary actions on complete neutralization. Such an alkali must possess a dissociation constant of K = about 10^{-9}, for $K = \frac{C'_{OH'}}{C_{MeOH}} = \frac{10^{-10}}{0.1} = 10^{-9}$ in which $C_{OH'}$ represents the hydroxyl ion concentration (assuming this to be 10^{-5}) and C_{MeOH} is the concentration of the unionized alkali molecules. An alkali fulfilling all these conditions is not easily found, but such a neutralizing solution can be readily prepared by mixing equivalent

[5] Magnesium carbonate is preferable to calcium carbonate on account of its solubility, neutralizing not only the outside portions but also the inner portions of the hide.

Digitized by Google

quantities of ammonia and ammonium sulphate, for the hydroxyl-ion concentration of such a solution yields according to the mass rule the desired value of $C_{OH'} = \frac{K \times C_{NH_4OH'}}{C_{NH_4}} = \frac{2.3 \times 10^{-5} \times 0.1}{0.1} = 2.3 \times 10^{-5}$, in which K represents the dissociation constant of ammonia (2.3×10^{-5}), $C_{NH_4OH'}$ the concentration of unionized ammonia molecules (which $^1/_{10}$N-solution is about 0.1) and C_{NH_4} the concentration of ammonia ions (which last, in $^1/_{10}$N-ammonium salt solution is also about 0.1). This mixture may be prepared by weighing out the calculated amounts of ammonia and an ammonium salt, but for economical reasons, a mixture may also be used, of ammonium sulphate and soda, according to the equation $2(NH_4)_2SO_4 + Na_2CO_3 + H_2O = 2N\ H_4OH + (NH_4)_2SO_4 + CO_2 + NA_2SO_4$.

In practice, a mixture of equal parts of ammonium sulphate and crystallized soda (each 2 per cent. of the weight of the leather) is recommended. Should this not be sufficient for the complete neutralization of the leather, then an additional mixture of 1 per cent. of ammonium sulphate and 2 per cent. of crystallized soda is added, for the ammonium sulphate formed in the first stage of the neutralization forms a retarding material for the ionisation of the ammonia present, so that the additional amount of ammonium sulphate can be reduced from 2 per cent. to 1 per cent.[6]

The process described produces a completely neutralized chrome leather without any bad secondary actions which arise when leather is over-neutralized. By this method, the fat-liquoring is simplified and the possibilities of spew on the finished leather lessened. Naturally, after neutralizing, the leather must be thoroughly washed with water. The mixture of equal parts by weight of crystallized soda and ammonium sulphate is also to be recommended in place of soda, borax, etc., for the partial detannization (stripping) of vegetable tanned leather which is to receive an after-tannage with one-bath chrome. The necessary amounts, for this purpose, may have to be greater than were given above.

[6] This method is preferable to the one published in the Tanners' Yearbook 1911, on account of being cheaper.

Digitized by Google

THE ANALYSIS OF VEGETABLE TANNING MATERIALS.[1]

By H. C. Reed.

The scope of this address, as the title indicates is rather a large one, and I have approached the subject with no feeling of overconfidence in my ability to present it in a manner that will enable you to bring to the practice of the methods the certainty of successful operation. Rather would I impress upon you the feeling that the precept of "practice makes perfect" is as difficult of demonstration in the particular field of the analysis of vegetable tanning materials, as in any other field of quantitative analysis, and yet I maintain that without practice, and strict adherence to the rules laid down, it is hopeless to expect concordance and the analytical consistency that is so important from the commercial side of the question.

To touch briefly upon the historical side of the subject, the first method for the estimation of tannin seems to be that of Sir Humphry Davy, by direct precipitation with gelatine and weighing of the tanno-gelatine precipitate. The method is of little if any value for a number of reasons, chief of which is the impossibility of properly washing the precipitate. Added to this is the fact that when too large a quantity of gelatine solution is added the tanno-gelatine precipitate is dissolved. It is probably for the latter reason that a method was suggested of using a standard gelatine solution with the addition of a little alum to flocculate the precipitate. The gelatine solution was first standardized by determining the exact amount required to precipitate all the tannin from a known tannin solution. The end-point was ascertained by testing the filtrate from the tanno-gelatine precipitate with both the gelatine and tannin solution, a precipitate with the former indicating an insufficiency of gelatine added and with the latter an excess. It was found, however, that at a certain point the filtrate gave precipitates with both gelatine and tannin, and this, with other equally valid reasons, such as the failure to obtain clear filtrates with solutions of certain tanning materials, forced the abandonment of the method.

[1] Lecture delivered before the students in the applied chemistry and tanning courses at Pratt Institute, Brooklyn, N. Y. Furnished for publication in the JOURNAL through the courtesy of Dr. Allen Rogers, Director.

Digitized by Google

It would be far too tedious, and result in no practical benefit to you, to go into the details of the many proposed methods for tannin estimation and the causes leading to their rejection. The use of basic dyes, alkaloids (quinine, strychnine, morphine and brucine), for precipitation of the tannin have given results of more or less interest but of little practical value, and metallic salts have also failed to give satisfactory results. The fault of all the methods dependent upon precipitation is incompleteness of precipitation in some instances, and throwing down of extraneous matters, such as coloring matters, gallic acid, etc., in others, which, combined with the fact that tannin is not of uniform chemical constitution, and varies in this respect with the source from which it is obtained, militates against any true comparison of the tannin content of one material as compared with the tannin content of another; although—as might be expected—such methods frequently give just comparisons of the relative values of two tanning materials containing tannin of the same class.

The methods thus far mentioned are all based upon precipitation of the tannin. Methods have been proposed of an entirely different nature based upon oxidation of the tannin and measurement of the amount of the oxidizing medium necessary to destroy the tannin. All oxidation methods are subject to the criticism that the amount of the oxidizing medium must be standardized to a tannin of known purity, such for example, as gallotannic acid. But here again we are confronted with the fact before mentioned of the difference in the chemical constitution of the different classes of tannin; and if we standardize our oxidizing agent against one tannin the results obtained with another fail to give a just comparison of the two. Again, it is difficult to prepare a tannin of absolutely known purity. Such methods are also complicated by the fact that substances other than tannin, present in all commercial tanning materials, are liable to oxidation, and a separate determination must be made of these substances and the amount deducted from the total oxidizible matters to obtain the tannin. The oxidizing mediums proposed were air, hydrogen peroxide in conjunction with lead peroxide—both requiring alkaline solutions of the tanning material—iodic acid and iodine. Of the various oxidation methods that known as the

Digitized by Google

Lowenthal, or permanganate method, is practically the only one that has proved of service, and although it is open to the objections previously mentioned as peculiar to all oxidation methods it is not without merit and practical value even at the present time. Briefly the method is based upon the titration of the tannin solution with a solution of permanganate of potash using indigo as an indicator, the indigo also to a degree controlling the oxidation. The permanganate solution is first standardized against a solution of pure gallotannic acid. A solution of the tanning material to be analyzed is then titrated in the same manner as the gallotannic acid, and another portion of the solution, from which the tannin has been removed with gelatine or hide powder, similarly titrated—the titration of the detannized solution being expressed in terms of gallic acid and the result deducted from the total titration to obtain the tannin. Gelatine and unchromed hide powder invariably give non-tan solutions that are too high and chromed hide powder is recommended. Various modifications of the permanganate method have been proposed, but it seems inadvisable to discuss them here. The original and modified methods may be found in detail in "Allen's Commercial Organic Analysis," Vol. 5.

We find the "indirect methods" of estimating tannin first appearing in a method which depended upon the difference in specific gravity of the tannin solution before and after removal of the tannin by means of hide powder. The calculation of the tannin content was based on the results obtained by trial which indicated that a one per cent. solution of pure gallotannic acid gave a specific gravity of 1.004 at 15° C. The method is not without value when used with judgment, although skill is required in the manipulation of the pycnometer, and the influence of temperature upon the specific gravity must be carefully calculated.

The Simand & Weiss method might be termed the father of the present method of tannin analysis. The method as originally suggested consisted in evaporating 100 cc. of a clear solution obtained by filtering the tannin solution, the residue being called the "total soluble." Two hundred and fifty cc. of the same solution was detannized by digesting and shaking with 1 gram of dry hide powder for several hours, filtering through linen, adding

Digitized by Google

2 grams more of the dry hide powder and digesting for a number of hours longer. Another 2 grams of the powder were added and after further digesting the solution passed through filter paper to a clear filtrate. One hundred cc. of this filtrate were evaporated and the residue, designated as "soluble non-tannin matter," deducted from the "total soluble" and the difference designated as "tanning matter absorbed by hide." It will be seen that in theory this method differs but little from the methods that are now official for both this country and Europe. In practice, however, improvements and refinements have been introduced since the method of Simand and Weiss first appeared, which have tended to greater concordance and accuracy, although in my personal opinion the transition stage through which the method passed before reaching its present level was largely retrogressive. I refer now to the method first suggested by Procter and known as the "filter-bell method." This differs from the method of Simand and Weiss in that the detannization of the tannin solution was effected by upward filtration of the solution through a tube or bell packed with dry hide powder, the percolation being effected through siphoning and the flow regulated by means of a pinch-cock. This method was adopted as official by the International Association of Leather Trade Chemists and continued as such for a number of years. It might be said here that the method is yet strongly advocated in certain quarters, notably by the German section of the International Association, and this despite the fact that the weight of evidence seems strongly opposed to the means of detannizing pursued. The inherent fault of the method is primarily due to the fact that fresh hide powder has an absorptive power for matters other than tannin, and owing to the method of manipulation the filter-bell method permits this absorption to an exaggerated degree. I feel that this is so important a point in consideration of methods of analysis of vegetable tanning materials that I desire to take a moment in explaining the modus operandi of the filter-bell method. The siphon-filter itself is of bell-shape, 7 cm. long by 3 cm. wide, and resembles a bottle with the bottom removed. The neck of the bottle is fitted with a rubber stopper through which passes the glass siphon tube, projecting slightly through the stopper into the bottle and

Digitized by Google

bent in the form of a siphon, the length of the tube being about 30 cm. The tube is fitted with a rubber tube and pinch-cock, as it is necessary to regulate the flow. The filter-bell is packed with from 6.5 to 7.5 grams of dry hide powder and great care must be exercised in filling, since too tight packing retards the flow of the solution and too loose packing results in channels, the liquor showing a tendency to pass up the sides and not through the powder. The use of cellulose with the hide powder largely overcomes this difficulty. After the bell is packed the hide powder is held in place by a piece of linen covering the open end of the bell fastened by a rubber band. I should have stated that the opening of the siphon tube within the bell is plugged with a bit of cotton to prevent the hide powder passing into or stopping up the siphon tube. The filter-bell is placed in a beaker and the tannin solution at first gradually added, permitting the wetting of the hide powder slowly and evenly by capillary absorption. So soon as the beaker and tube are filled with the solution the siphon is started by sucking gently on the end of the siphon tube, and the detannized solution allowed to drop at the rate of one drop in two seconds. The first 30 cc. is discarded and the following 60 cc. collected, from which the 50 cc. are pipetted for evaporation for non-tannins. An examination of the hide powder in the filter-tube after an analysis has been run will disclose that the bottom layer of the powder is very thoroughly tanned but by far the greater part of the powder is practically untanned. In other words that portion of the powder first in contact with the tannin solution absorbs practically all the tannin thus necessitating the passage of detannized solution through fresh, untanned hide powder. Abundant proof has been offered to the effect that the non-tannin matters of tannin solutions contain substances more or less readily absorbable by untanned hide powder, and the effect of the passage of the detannized solution in the filter-bell method through the fresh hide powder in the upper portion of the bell is the abstraction of a very appreciable amount of these substances and a corresponding diminution in the amount of non-tannin matters found by evaporation of the 50 cc. selected. The use of chromed hide powder (which will be treated of more fully later) will show an even greater absorption of non-tannin

Digitized by Google

matters by the filter-bell method than unchromed powder. The fault of the filter-bell method is therefore inherent in principle, and no successful method has been proposed, and probably from the very character of the manipulation involved can never be proposed—to overcome the fault. I have purposely gone more deeply into the details of this method in order to disabuse your minds of any feeling of confidence in its value, for I admit that on the face of it it seems plausible and attractive. Let me say that its attractiveness is pronouncedly greater for the commercial interests engaged in the sale of tanning materials than in the purchase of them. The filter-bell method invariably gives lower non-tannins and consequently higher tannin than does the shake method, the details of which I am now approaching.

As I have mentioned before it seems unfortunate to say the least that a digression from the method suggested by Simand and Weiss should have occurred. The shake method as we now have it is but a safe and sane development of this older method. It is of interest that the chemists of this country never adopted the filter-bell method. Following the lines laid down by Simand and Weiss, Yocum, in the year 1894, suggested the use of a shaking machine to hasten the detannization, it being found that ten minutes shaking would accomplish the desired result, as compared with many hours consumed in the Simand and Weiss method. Much trouble, however, was experienced from lack of concordance in the non-tannin figure, which could be traced directly to lack of uniformity in the quality of the hide powder. This lack of uniformity could be attributed to differences in the absorptive powers of different powders and to soluble matters contained therein. This evil was later corrected by the use of chrome salts.

I have almost entirely refrained up to the present from touching upon any phase of the analysis of vegetable tanning materials that does not deal with the question of the removal of tannin or detannization of the tannin solution. I believe that it will be best to temporarily digress and take up the subject of analysis in the order laid down by the Official Methods of Tannin Analysis.

There are two methods known as "Official," one adopted by the American Leather Chemists Association and the other by the International Association of Leather Trade Chemists. The

Digitized by Google

two methods differ somewhat in detail but very little, if at all, in the results given. I will explain the Official Method of the A. L. C. A. and later show in what particulars the method of the I. A. L. T. C. differs.

Referring to the booklet issued by the A. L. C. A. we find:

I. CRUDE MATERIALS.

(1) *Moisture Determination*:

Upon receipt of the sample, grind promptly and dry 10 grams in the manner and for the period specified for evaporation and drying in extract analysis.

In explanation of this I would say that it is presumed that the sample furnished the analyst is truly representative, and if so should contain the amount of water that the lot from which it was drawn contained. For this reason it is imperative that as little moisture as possible be lost in grinding.

(2) *Preparation of Sample for Extraction*:

Sample must be dried at a temperature not exceeding 60° C., and then ground to such a degree of fineness that the entire sample will pass through a sieve of 20 meshes to the inch (linear).

The idea of drying at a temperature not exceeding 60° C. is to prevent any possible alteration in the character and composition of the material which might result from higher temperatures. The degree of fineness of the ground material is specified mainly with a view of having it sufficiently fine to permit of ready extraction. Coarse particles will naturally extract more slowly than finer, and consequently the rapidity of extraction is dependent upon the coarsest particle. With materials that yield their extractive matter slowly, 20 meshes to the inch is none too fine a preparation. I would impress upon you the necessity of rigidly adhering to the rule of passing the "entire" sample through the sieve, as it is only by doing so you may hope to have an absolutely uniform sample for extraction.

(3) *Amount of Sample and Proportion of Water for Extraction*:

For fresh materials the amount of sample and proportion of water for extraction should be such as to give between

Digitized by Google

0.35-0.45 gram tannin per 100 cc. of solution. For spent materials this proportion should be aproximated as closely as practicable.

The range of 0.35 to 0.45 gram tannin per 100 cc. of solution has been selected as suitable for the amount of hide powder used in detannizing. It is true that certain tannin solutions are more readily detannized than others, and therefore more hide powder is used in some instances than is absolutely necessary. On the other hand it sometimes happens that the specified amount of hide powder to the range of tannin is insufficient to remove the last trace of tannin from the solution. This, however, happens very infrequently, and you must understand that in analyses of the character of those we are dealing with it is most important that the method should be such as to give concordant results between analysts. In the particular instance of the prescribed range of tannin I am convinced that greater uniformity would result from a narrowing of the range. It is undoubtedly true that if one analyst uses a dilution representing but 0.35 gram tannin per 100 cc., greater diffences will be shown that if both tannin per 100 cc. and another dilution representing 0.45 gram had used a dilution containing the same amount of tannin. The explanation is very similar to the one given in the case of the filter-bell method. If the hide powder present is in excess of the amount necessary to complete detannization then the superfluous, untanned powder shows a tendency to absorb non-tannin matters. The higher the proportion of hide powder to the tannin present the lower the non-tannins, and vice versa.

The amount of a material taken for extraction that will give a solution of the required tannin strength is a question of information gained from experience. The amount of water present will influence the weight to be taken of materials of different samples of the same material. It is not uncommon to extract but 10 grams of a mangrove bark to the liter of water, and 50 grams of a chestnut wood.

(4) *Extraction of Sample*:

Extraction shall be conducted in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, and shall be continued until a portion tested with gelatine salt solution fails

Digitized by Google

to give a precipitate. Five hundred cc. of the first portions of extractive solution should be removed and not subjected to further heating. A thin layer of cotton must be used in order to prevent fine material passing over.

I will not undertake to describe the extraction apparatus other than to say that all such apparatus used in this country are of a Soxhlet or modified Soxhlet type. Whatever the type it must be such as to allow the withdrawal of 500 cc. of the extractive solution so that it may not be further subjected to the influence of high temperature. Experiments have proved that continued heating of solutions of tannin results in conversion of tannin into non-tannin and insoluble matters, and that in this respect the more readily extractible tannins are the most sensitive. Hence if the extractive first coming over is removed so as to prevent the destructive action of prolonged boiling, tannin is conserved. The gelatine-salt solution is composed of 1 per cent. gelatine and 10 per cent. salt. A drop of the solution should be added to several cubic centimeters of the extractive solution, cloudiness indicating that the tannin has not yet been entirely removed.

(4A) *Sumac and Kindred Materials*:

Put the material (the amount should be such as to give between 0.35-0.45 gram tannin per 100 cc. of solution) in a form of apparatus that permits the removal of the extractive solution from the influence of sustained high temperature, cover it with water and allow to soak one hour. Then extract by collecting 2,000 cc. of the extractive solution outside through lower tube, in from six to eight hours. Let the extractive solution stand over night and analyze the following day by the Official Method for Extracts.

With such materials as sumac, myrobalans, valonia, divi-divi, etc., which are by nature readily extracted and contain tannins that are excessively prone to destruction by prolonged high temperature, it has been found that better results are obtained by collecting the entire extractive outside.

I would like to remark here that most of the extractors used in this country are made of copper. There is no doubt but that copper has a detrimental effect upon tannin solutions, especially

Digitized by Google

in continuous extraction where the solution is boiled in the copper vessel. I would advise that the interior of all copper extractors be tinned, for my experience proves that this aids materially in preventing tannin loss. Glass apparatus is of course the most desirable, but it is far too fragile. Personally I am far from satisfied with the method as it stands. Too wide divergences occur between analysts, which I believe can be directly attributed to differences in degree of extraction. The gelatine-salt test is not altogether reliable. For example, in the extraction of chestnut wood it is practically impossible to arrive at a point where the extractive solution fails to give a positive test for tannin. The true explanation probably lies in the fact that certain substances other than tannin are extracted which precipitate with gelatine, and in all likelihood these are of the nature of soluble cellulose products. The American Leather Chemists Association has not seen fit to adopt a method which was proposed with the idea of defining the time of extraction, and limiting the amount of heat applied by regulating the speed of extraction. It would seem as though some such hard and fast rule would at least conduce to better uniformity in results, which to my mind is the factor of paramount importance. Even if the exact tannin content of a given material is not ascertained with absolute correctness, yet if we can agree on a tannin content the status of the commercial value of the material can be fixed, and if bought and sold on the tannin unit the value of the unit will very quickly adjust itself to the analytical tannin content. Perhaps I am looking at the question from the commercial aspect to the exclusion of the theoretical, but in defense I would claim that the methods of analysis owe their existence in large measure to the demand for a uniform basis upon which to buy and sell.

(5) *Analysis*:

After extraction and dilution, solutions must be heated to 80° C., and analysis conducted as per Official Method for Extracts. In case of weaker dilutions than the Official Method specifies, the amount of hide powder must be reduced in proportion to the reduction of tannin.

Ten grams of the air-dried sample should be dried as in (1) to determine moisture content of the portion extracted

Digitized by Google

and the analysis calculated and reported upon a "dry" basis. The tannin in fresh materials should also be reported on the basis of the moisture content of the sample "as received."

The reason for re-heating the solutions to 80° C. after extraction is principally from the fact that the strong extractive solution first coming over deposits insolubles which in a dilution of official strength and with warming go into solution. The reference to "weaker dilutions than the Official Method specifies" principally refers to spent materials. It is customary to extract 50 grams of spent tanning materials in 1 liter of water and to proportion the amount of hide powder to the amount of tannin present, which almost invariably means a reduction in the quantity of hide powder below the 12 to 13 grams called for by the official dilution, since a spent material containing 7 per cent. of tan (which would be equivalent to 0.35 gram tannin per 100 cc. of solution) would be very extraordinary. It is the custom of many analysts to report spent tans on the absolutely dry basis and calculate the tannin content on the original fresh material by multiplying by three-fourths, on the assumption that the average water content of the new material plus the loss of weight by extraction is equivalent to one-fourth of the dry spent.

II. ANALYSIS OF EXTRACTS.

(6) *Amount and Dilution for Analysis*:

Fluid extracts must be allowed to come to room temperature and weighed in stoppered weighing bottle. Such quantity shall be taken as will give from 0.35-0.45 gram tannin per 100 cc. of solution. Dissolve in exactly 900 cc. of distilled water at 80° C., and make up to mark after standing not more than 20 hours, nor less than 12 hours. Temperature must not go below 20° C.

The reason for "allowing fluid extracts to come to room temperature" before weighing is obviously on account of the differences in weight at different temperatures. I presume that we should be cautioned to weigh our residues after evaporation and drying with the room at the same temperature as when the extracts were weighed out. The use of the stoppered weighing bottle is to prevent evaporation during weighing. I have already

Digitized by Google

referred to the question of the amount to take for analysis. The specification to dissolve in exactly 900 cc. water at 80° C. is apparently an innocent provision that can be readily complied with, but with solid and dry extracts it is not so feasible as it might seem. The difficulty really arises in a means of introducing the extract into the flask. One might suggest the use of a beaker holding 900 cc. and submersion of the weighing bottle in the 900 cc. of water and keeping at the temperature of 80° C. on the water-bath, stirring till dissolved. The awkwardness of such a procedure will appeal very strongly to one who has a large number of extracts to dissolve in a limited time. I trust that this paragraph of our Official Methods will shortly be subjected to revision. In my estimation as good a method as any for dissolving solid extracts is to weigh out in a beaker capable of holding 100 cc., dissolving directly on the water-bath in 100 cc. of water and transferring to the flask by washing through a funnel with water at say 85° C. Liquid extracts could be transferred directly to the flask in a similar manner, dissolving on the water-bath being unnecessary. Flasks can be roughly graduated to 900 cc. by marking with diamond ink. As our method calls for a gradual cooling of the solution over night the provision to stand between 12 and 20 hours before making to mark is easily followed. Considerable work has been done along the lines of rapid cooling of solutions in order to effect a saving in time taken for analysis; and such a saving is very desirable, although the trials have shown less uniformity in results from rapidly cooled solutions with extracts that contain higher insolubles. With approximately clear tannin solutions there is very little difference shown between the results from the Official and rapid-cooling methods. A change to a rapid-cooling method would also necessitate a change in the chroming of hide powder for analysis, which will be referred to later. Before leaving this paragraph of the Official Methods I would point out that a provision should be inserted requiring a thorough mixing of a liquid extract before weighing out for analysis. Certain fluid extracts upon standing will deposit considerable insolubles which unless distributed throughout the sample will lead to the weighing out of a portion that is not representative. The provision to

Digitized by Google

not allow the temperature of the solution to go below 20° C. is to prevent the formation of insolubles, and will be discussed under "Soluble Solids."

(7) *Total Solids*:

Thoroughly mix solution, pipette 100 cc. into tared dish, evaporate and dry as directed under "Evaporation and Drying."

No explanation of this section seems necessary here. I would suggest that the most particular attention be paid to the accuracy of the pipette, and believe that a pipette certified by the Bureau of Standards at Washington is advisable. In general it is wise to standardize the liter flasks, as they are by no means always accurately graduated.

(8) *Soluble Solids*:

To 1 gram of kaolin in a beaker add 75 cc. of solution; stir and pour on a 590 S. & S. 15 cm. plaited filter-paper; return filtrate to paper for one hour, keeping filter full. At the end of an hour pour solution from filter or remove with pipette. Bring 800 cc. of solution to 20° C.; refill the filter with this solution and begin to collect filtrate for evaporating and drying so soon as filtrate comes clear. Keep filter full. Evaporate and dry the first 100 cc. of filtrate, as per "Evaporation and Drying."

Funnels and receiving vessels must be kept covered during collection of filtrate for evaporation.

The kaolin used should be free from all soluble salts, and great care should be observed to see that this is so. Frequently it is necessary, and perhaps always advisable, to wash the kaolin with hydrochloric acid, and if this is done it must be well pulverized again after drying. The filter-paper selected by the A. L. C. A. is the one that experience has shown to be best adapted to the purpose, giving more consistently clear filtrates and showing less absorption for tannin than any of the many others that have been tried. You will understand that cellulose has a not inconsiderable attraction for tannin, and the purpose of returning the filtrate to the paper for one hour is to satisfy the affinity of the paper for tannin as well as to fill the pores of the paper with

Digitized by Google

the kaolin thereby forming a mat which, with the insolubles contained in the tannin solution, prevents the passage of the finely divided and often colloidal insolubles. The object of keeping the filter full is to prevent the disturbing of the kaolin mat, which when exposed by too great lowering of the solution on the paper is liable to cause roiling when the filtrate is returned.

The solution upon the paper may be poured off at the expiration of the hour, or, what is perhaps better, removed with a pipette or large-bulb dropper. Whatever the method employed care must be taken not to disturb the kaolin film. If the original solution is not at 20° C. it must be cooled down to the temperature, and water at 15° C. is in my estimation the best medium. The flask should be constantly agitated while cooling. As mentioned under (6) the temperature of the solution must not go below 20° C. at any time, as insolubles are formed which will not in certain cases thoroughly redissolve upon warming to 20° C. The solution at 20° C. is then poured upon the paper, and the start made in collecting the filtrate as soon as it comes clear. With some extracts, notably unclarified quebracho, it may be necessary to allow the solution to filter for some little time before collecting, and sometimes it is practically impossible to obtain a filtrate that is not slightly opalescent.

(9) *Non-Tannins*:

A quantity of hide powder sufficient for the number of analyses to be made shall be prepared in the following manner: Digest with 10 times its weight of water till thoroughly soaked. Add 3 per cent. of chrome alum in solution. Agitate by either shaking or stirring occasionally for several hours and let stand over night. Wash by squeezing through linen, continuing the washing until the wash water gives no precipitate with barium chloride. Squeeze the hide, using a press, if necessary; so that the wet hide will contain between 70 and 75 per cent. of water. Use approximately 20 grams of wet hide for moisture determination. Add to 200 cc. of the original solution such quantity of the wet hide as represents from 12 to 13 grams dry hide. Shake for ten minutes in some form of mechanical shaker and squeeze immediately through linen. Add 2 grams kaolin to the fil-

Digitized by Google

trate, stir and filter through folded filter (No. 1F Swedish, recommended) of size sufficient to hold entire filtrate, returning until clear. Evaporate 100 cc. of the filtrate. The weight of the residue must be corrected for the dilution caused by the water contained in the wet hide powder.

NOTE.—In order to limit the amount of dried hide powder used, determine the moisture in the air-dried powder and calculate the quantity equal to 12½ grams of actual dry hide powder. Take any multiple of this quantity according to the number of analyses to be made, and after chroming and washing as directed, squeeze to a weight representing 70 per cent. to 75 per cent. water. Weigh the whole amount and divide by the multiple of the 12½ grams of actual dry hide powder taken to obtain the weight of wet hide powder for 200 cc. of solution.

The non-tannin filtrate must not give a precipitate with a 1 per cent. gelatine 10 per cent. salt solution.

The question of non-tannin determination might be said to transcend in importance any other single item in the analyses. The hide powder used by members of the American Association, and largely used now by members of the International Association, is that known as the "American Standard Hide Powder." Our method contains no specifications as to the acidity of the hide powder, and I believe that this is a mistake. The proportion of acid in a hide powder makes no little difference in the resulting non-tannins, which is evinced in the analysis itself in the appearance of the non-tan filtrate. Too little acid in the powder is liable to give cloudy or colored filtrates with solutions of certain tanning materials, mangrove bark solutions notably offending in this respect. Too much acid on the other hand gives a powder which swells to a degree that makes proper washing difficult and if present above a certain amount will give high non-tans. As hide powder of the same acidity does not act the same in respect to its absorptive power for solutions of different tanning materials, you will readily comprehend the difficulty in adjusting the acidity so as to have a powder that will answer for detannizing any and all solutions. Theoretically it must be sufficiently acid to give proper non-tannin filtrates with the most difficultly detan-

Digitized by Google

nized materials, while at the same time we must not lose sight of the fact that with easily detannized solutions the non-tans are reduced by an excess of acid in the powder. With hide powder of the character of the "American Standard," prepared and used according to our Official Method, an acidity requiring 1 cc. N/10 alkali to 1 gram of the powder is approximately of correct proportion. The powder should be of as uniform a preparation as possible, and especially should it be free from lumps, to insure an even distribution of the chromic oxide and the exposure of equal surface to the liquor to be detannized. Until a few months ago the hide powder was soaked in twenty-five times its weight of water, but the method has been changed to read ten times. Three per cent. (estimated on the weight of the air-dry hide powder) of chromic alum in solution is added and the wet mass agitated, frequently at first and occasionally for several hours, and allowed to stand over night. It is well to begin the chroming about noon thus permitting time for thorough agitation during the remainder of the working day. The washing of the powder should be started early the following morning, and continued until the wash water gives no test for sulphates with barium chloride. Washing should be done with distilled water, and is necessary not only for the removal of sulphates set free by the reduction of chrome alum to chrome oxide but for the cleansing of the hide powder from soluble organic matters contained. My method of washing differs, I believe, from that employed by most of my confreres and does not lend itself readily to description. The linen cloth, well wet, is firmly attached by means of a stout rubber band to the rim of a bell-jar, supported by inverting the bell in a specially made tripod, the rim of which fits under the rim of the bell. The linen cloth is bellied down within the bell-jar, which is fitted with a stop-cock at the bottom. The wet mass of chromed hide powder is thrown upon the cloth, and, the stop-cock of the bell-jar being closed, the cloth is grasped and pulled upward, causing a vacuum within the bell and forcing the water through the cloth. Distilled water is poured upon the powder and the operation repeated. When adding the water it is well to stir the wet mass with the hand, breaking up the caked portions. I have gone into a somewhat lengthy explanation of

Digitized by Google

this method of washing as I believe it of no inconsiderable avail in hastening a rather tedious operation. After washing is finished the wet hide is squeezed, usually in a press, so as to contain from 70 to 75 per cent. water. With practice this is not difficult, and it is the custom of many analysts, and excellent practice too, to have always a definite amount of water in the wet hide used for analysis. This may be accomplished by the knowledge gained from actual trial that a given amount of the original dry hide powder when washed and squeezed will, with a definite wet weight, contain a fixed and definite amount of water. Experience will teach one to squeeze the wet hide a trifle below the required weight to which it can be brought back by the addition of distilled water. It is perhaps unnecessary to point out that one must be careful in washing not to lose hide powder thereby upsetting the calculation. Experience, and adherence to the rule laid down in the "Note," will also teach how much of the wet hide powder of a definite water content will be necessary to give from 12 to 13 grams of dry hide per 200 cc. of solution. The per cent. of water in the wet hide is of course calculable from the data already in hand, but it is well as a precautionary measure to weigh out approximately 20 grams for moisture determinations as the method instructs. The mechanical shaker now almost universally used is of the revolving type. Quart bottles, the wide-mouth variety, with rubber stoppers, are the kind generally used. The speed of the shaker, or the revolution, must be so adjusted as to permit the throwing of the hide powder from end to end of the bottle. Sixty to sixty-five revolutions per minute with the inner side of the bottle approximately one inch from the axis of the shaker will accomplish a proper agitation. The method does not say that the shaking should be done immediately upon adding the hide powder to the liquor, and should be corrected so to read. Immediately upon the expiration of the ten minutes of shaking the wet mass should be thrown upon the linen cloth, squeezed, the liquor stirred with 2 grams of kaolin and filtered through paper. I would highly recommend the No. 1F Swedish paper, folded and of size to hold the entire quantity of the filtering solution. The filtrate must be returned until clear and must not give a positive test with the gelatine-

Digitized by Google

salt solution before mentioned. I would remark that there is a certain rigidity to the method that I am thankful to say is only infrequently embarrassing but which must be the occasion of some action by the Association in the near future. It sometimes happens that a tannin solution of official strength will give a non-tan filtrate showing a test for tannin with gelatine-salt solution. If we alter the dilution, the amount of hide, or report the non-tannins after showing test for tannin, we are disobeying the law. Pending the settlement of the question I am unwilling to advise you further than to remark that if the specified amount of hide powder to an official dilution fails to detannize completely it is in itself *prima facie* evidence that the material under analysis is of lesser value than, for example, a material of like nature that will detannize. In other words, my personal view is that the evidence of the gelatine-salt test should be subservient to the fact that all other conditions of the method have been complied with. One hundred cc. of the filtrate are evaporated and corrected for the dilution caused by the water contained in the wet hide. Thus if we should use 50 grams of wet hide containing 75 per cent. water we would increase the 200 cc. by diluting with 37.5 cc. of water from the hide (75 per cent. of 50 grams), making a total of 237.5 cc., and the correction would be the factor of 237.5 ÷ 200, or 1.188 which the residue must be multiplied by to give the actual figure that would obtain had the hide powder been absolutely devoid of moisture.

(10) *Tannin*:

The tannin content is shown by the difference between the soluble solids and the corrected non-tannin.

This requires no explanation in itself, but it might be well to remark here that if there is one consideration above all others that makes this method of tannin determination of weight, and will keep it in a commanding position, it is by reason of its similitude to actual tannery practice. Other methods have failed largely because this parallel is missing. The tanner desires to know how much of a given tanning material, call it tannin or what you will, goes into his hide to make leather, and the analysis to the best of its ability, deviating from the tanner's usage only

Digitized by Google

in so far as is necessary to meet laboratory conditions, expresses this.

III. ANALYSIS OF LIQUORS.

(11) *Dilution*:

Liquors must be diluted for analysis so as to give as nearly as possible 0.7 gram solids per 100 cc. of solution.

(12) *Total Solids*:

To be determined as in Extract Analysis.

(13) *Soluble Solids*:

To be determined as in Extract Analysis.

(14) *Non-Tannins*:

To be determined by shaking 200 cc. of solution with an amount of wet chromed hide powder, containing 70 per cent. to 75 per cent. moisture, corresponding to an amount of dry hide powder shown in the following table:

Tannin range per 100 cc.	Dry hide powder per 200 cc.
0.35—0.45 gram	9— 11 grams
0.25—0.35 gram	6.5— 9 grams
0.15—0.25 gram	4—6.5 grams
0.00—0.15 gram	0— 4 grams

Solutions to be shaken for non-tannins as in Extract Analysis; 100 cc. must be evaporated as in Extract Analysis.

In the analysis of tannery liquors the fundamental principles are the same as in the analysis of extracts although differing somewhat in detail. The original dilution of a liquor must be such as to give approximately 0.7 gram of solids per 100 cc. of solution. Liquors, in all but exceptional cases, are pipetted for analysis dilutions, not weighed. The amount of a liquor required for the analysis solution giving 0.7 gram solids per 100 cc. is so large that any small error in pipetting is insignificant. Liquors should, however, be calculated on weight and not volume, but as the barkometer strength of a liquor must practically always be taken, and the reading shows at once the specific gravity, the weight of liquor taken for analysis is readily calculated by multiplying the volume by the gravity. The temperature of the liquor must always be taken into account in the barkometer readings and there are tables to show the degrees barkometer to add or subtract from the reading to calculate the actual finding to a uniform

Digitized by Google

temperature of 60° Fahrenheit. Most liquors can be diluted with cold water and analyzed immediately, thus effecting a saving in time as compared with extract analysis. With exceptionally heavy liquors, which are not so frequent in this country as on the Continent, it is advisable to dilute in water at 80° C. after the manner proscribed for extracts, cold water not producing the degree of solubility of hot. Total solids, soluble solids, and insolubles are determined as in extract analysis. The non-tannin estimation on liquors differs from the determination in the case of extracts in that the amount of hide powder used is less in proportion to the tannin content of the solution analyzed, and graded as the necessity demands where the dilution is based on a definite quantity of solids to a definite quantity of water rather than on a definite quantity of tannin to a definite quantity of water. The reason for using a smaller amount of hide powder to the same amount of tannin in liquor analysis as compared with extract is due to the fact of the greater acidity of the former as compared to the latter, and, just as in the case of more acid hide powders there results better detannization, so with more acid in the solution to be detannized there is shown more ready absorption of tannin by the hide. To be absolutely true the analysis must return as matters absorbable by hide nothing but tannin; to be just it must return as tannin as little matters as possible absorbable by hide other than tannin. This is what the analysis aims at. Practically it is impossible to accomplish complete absorption of tannin by hide powder without an accompanying absorption of some small amount, sometimes more and sometimes less, of non-tannin substances. And indeed this is true in the actual practical tanning process, as analysis of leather itself will prove, although I would not be understood as claiming that this is an argument in favor of a method of analysis which returns as tannin matters that could not be properly designated as astringent. On the contrary I would cite my opinion, elsewhere expressed, of the filter-bell method, my very reason for condemning which is based on the well-established fact that the hide powder, from the modus operandi, removes the non-tans in excessive amount. The amount of wet hide powder used in liquor analysis is therefore reduced from the equivalent repre-

Digitized by Google

senting 12 to 13 grams of dry per 200 cc. of solution in extract analysis to the equivalent representing 9 to 11 grams of dry per 200 cc., and with dilutions of liquors containing less amounts of tannin a proportional reduction in the quantity of hide powder is made as the table shows. The correct adjustment of the solids per 100 cc. and the proportions of hide powder to use must be left to the experience of the individual analyst. A single experience in the analysis of a series of liquors from a tannery will be a sufficient guide to a subsequent series from the same tannery, but the experience gained from the liquors from one tannery is not by any means reliable for the liquors from another.

IV. EVAPORATION AND DRYING.

(15) *Evaporation and Temperature*:

All evaporations and dryings shall be conducted in the form of apparatus known as the "Combined Evaporator and Dryer," at a temperature not less than 98° C. The time for evaporation and drying shall be 16 hours.

The method for evaporating tannin solutions and drying the residues has always been the subject of considerable controversy. The combined evaporator and dryer owes its existence to a natural evolution. Formerly the evaporation was done on a water-bath and the drying in a hot-air or steam-oven. The great objection to the water-bath for evaporating lies in erosion of the glass dishes from impinging of the steam on the bottoms, the change in weight making accurate analysis well-nigh impossible. With Jena or Nonsol glass the alteration in weight is not so evident, but there is always an element of uncertainty. This brought about the use of a hot plate instead of a water-bath, and since the transferring of the dishes to an oven for drying the residues after evaporation entailed another operation, the idea of covering the hot plate to form a drying-oven suggested itself, and thus later developed into "jacketing" the hood for steam to increase the temperature. The resulting combined evaporator and dryer is a most serviceable apparatus, and with condenser attachment to furnish distilled water effects no little economy in the laboratory. Perhaps from a theoretical standpoint a vacuum dryer is superior, but there are certain objections to its

Digitized by Google

use which are not apparent on first thought. Under vacuum evaporation there is always danger of the evaporation liquor sputtering. On the other hand there is no doubt but the rapidity of evaporation combined with reduced temperature tends to less oxidation of the residues while shortening the time of analysis.

(16) *Dishes*:

The dishes used for evaporation and drying of all residues shall be flat-bottomed glass dishes of not less than 2¾ inches diameter nor greater than 3 inches in diameter.

The glass dishes used should be as described, and I believe the 2¾ inch dishes are preferable as allowing a greater capacity to the evaporator and dryer and exposing a smaller film area to the influence of oxidation. I feel that it would be preferable for the method to specify a dish of a uniform size rather than to allow the present latitude. Porcelain dishes, nickel dishes and platinum dishes have been tried, the two former having no advantage over glass and the latter being out of the question by reason of cost. The glass dishes should be numbered and the tare checked frequently. When first used the dishes will alter in weight rather considerably, after which the change is slight and gradual barring accidental chipping in handling.

I might here say a word relative to the weighing of residues. When the dishes are taken from the evaporator and dryer they should be placed immediately in desiccators, and my preference is most decidedly for individual desiccators. Either suplhuric acid or calcium chloride may be used in the desiccator, but I much prefer the former. About one-half hour should be allowed for cooling of the dishes before weighing, and the dishes transferred from the desiccator to the pan of the balance with small tongs or pincers, protected with rubber to prevent breaking of the dishes. The weighing should be as rapid as accuracy permits, and I doubt whether any other class of laboratory work develops more exact and rapid weighing than does the analysis of tanning materials. Tannin residues take on weight rapidly when exposed to moist air, and it is almost impossible to weigh accurately by the swing. The balance used should, perforce, be of the rapid type; preferably, in my opinion, with the beam graduated to 10 milligrams, thus doing away with the 5 milligram weight.

Digitized by Google

I have already called attention to the fact that there are two official methods for tannin estimation, the one official for this country, that of the American Leather Chemists Association, and the other official for Europe, that of the International Association of Leather Trades Chemists. What difference, if any, exists between the two methods?

The strength of the tannin infusion used for analysis is identical in both methods, viz., 0.35 to 0.45 grams tannin per 100 cc. In extraction the influence of temperature in the destruction of tannin is recognized by the instruction that "the greater part of the tannin must be removed at a temperature not exceeding 50° C. with 500 cc. of water, and continued until 1 liter in all has been extracted, with boiling water." The percolation should last not less than three hours, and the Koch and Procter extractors are mentioned. It seems exceedingly doubtful whether the method will remove all the tannin. Personally I do not believe it will, except with readily extractable materials such as fall under Section 4A of our Official Method and designated as "Sumac and Kindred Materials."

The I. A. L. T. C. Method says in respect to dissolving liquid extracts that they shall be weighed in a basin or beaker and washed into the liter flask with boiling distilled water. In some particulars I believe this to be better than the A. L. C. A. Method. I have never been an advocate of weighing out extracts in a weighing-bottle and feel that it is an entirely unnecessary refinement. The extract can be more easily washed out of a beaker than a weighing-bottle, and if the analyst is not sufficiently expert to weigh out with a degree of rapidity that will not affect the ultimate tannin figure he should learn to do so before undertaking tannin analysis. In respect to the use of boiling water to dissolve the extract rather than water at 80° C., which the American method calls for, I am not prepared to advocate the superiority of one over the other except to say that the former has the advantage in point of effecting more rapid solubility. The I. A. L. T. C. method states that sumac and myrobalan extracts should be dissolved at lower temperature. Concerning solid extracts the International method recommends dissolving in a beaker with stirring by adding successive portions of boiling

Digitized by Google

water, decanting into the liter flask. This is very similar to the method I have suggested as superior to the specifications of the A. L. C. A. method.

The I. A. L. T. C. method calls for optically clear soluble solids filtrates, and the Berkfeld filter-candle, S. & S. No. 590 paper, or any other paper may be employed for the filtration. When the S. & S. No. 590 paper is used no correction is made for the absorption of tannin by the paper provided 250 to 300 cc. of solution is passed through the paper before collecting the quantity required for evaporation. If other papers are employed a test is made to ascertain the absorption power of the paper for tannin by filtration of 500 cc. of the same or a similar tanning material, estimation of the solids contained in the filtrate, and re-filtration of the clear filtrate and determination again of the solids, the difference being the tannin absorbed by the paper, which is used as a correction factor. The Berkfeld filter is made of a porous, infusorial earth, and is used with vacuum. The candle has a hollow core and this being connected with the vacuum chamber the immersion of the candle in the tannin solution forces the solution through the candle from whence the filtrate is forced to the collecting vessel. I will not go into the pros and cons of this method of filtration except to say that it has been tested by the American Association and in its opinion found wanting. The candle is used again and again, which means cleansing between each filtration. Brief mention might be here made of a method of filtration which emanated from myself. This has been known as the asbestos-kaolin method, and consists in an asbestos mat superimposed upon a perforated, porcelain filter-plate in a funnel, the neck of the funnel entering a vacuum chamber. The tannin solution, stirred with kaolin, is thrown upon the asbestos mat, the kaolin serving to fill up the interstices and thus to make a filtering medium that will retain the finely divided precipitates. The method has the advantage of practically always giving optically clear filtrates and with a degree of rapidity not obtainable with paper filtration. It has the disadvantage, especially where a number of analyses are to be made at one time, of requiring the installation of a rather complicated apparatus, and this detriment has prevented its adoption. With

Digitized by Google

asbestos and kaolin the absorption of tannin is very slight. In all filtration methods where vacuum is used it is imperative that the vessel in which that portion of the filtrate is collected for evaporation be disconnected from vacuum pump itself. In other words, the vacuum should be formed in the collecting vessel and closed in during filtration, otherwise there will be an appreciable increase in soluble solids by loss of water from evaporation.

The I. A. L. T. C. method is more specific than our own as to the acidity of the hide powder, which shall require not more than 5 cc. of N/10 alkali for neutralization of 6½ grams of the dry powder. In the chroming of the powder, crystallized chromic chloride ($Cr_2Cl_6 12H_2O$), made basic with sodium carbonate, is used instead of chrome alum as in the American method. The International method calls for 2 per cent. of chromium chloride and the American for 3 per cent. of chrome alum ($Cr_2(SO_4)_3K_2SO_4 24H_2O$). The former corresponds to 0.565 gram of chromic oxide (Cr_2O_3) per 100 grams of powder and the latter to 0.457 gram of chromic oxide per 100 grams of powder, thus making the hide used in the I. A. L. T. C. method somewhat more highly chromed than in the A. L. C. A. method. As the reduction to chromic oxide of the basic chromium chloride sets free chlorides these are tested for in the wash water with potassium chromate and silver nitrate. The amount of water left in the wet-chromed powder is the same in both methods, but the International method before shaking the tan solution and hide powder calls for the addition of sufficient distilled water to make the evaporation of 60 cc. of the filtrate correspond to 50 cc. of the original solution, or in other words, instead of employing a correction factor for the non-tans these are automatically corrected in the analysis itself. I should have perhaps made note of the fact that 50 cc. are usually taken for analysis by the International method instead of 100 cc. required by our method. The chroming of the hide powder in the I. A. L. T. C. method is conducted by agitating in a churn for one hour and proceeding with the washing immediately.

In the analysis of liquors the I. A. L. T. C. method is more drastic than ours in requiring the proportion of 0.35 to 0.45 gram tannin per 100 cc. of solution, weak liquors being concen-

Digitized by Google

trated before analysis in order to attain the tannin concentration. If for any reason it is not possible to concentrate sufficiently the 6½ grams of dry powder used must not be varied from. Personally I am entirely opposed to a method requiring evaporation of the liquors as leading to alterations in their character which would very probably be reflected in the analysis.

The International method requires rapid cooling of the solution immediately after dissolving to a temperature between 15° and 20° C., while the American method requires standing over night. Much experimental work has been done by our Association with the end in view of substituting a rapid-cooling method for the over-night method, but with the conclusion that the former, with materials like quebracho, hemlock and oak bark containing considerable insolubles, leads to wider variations in results than the latter. The difficultly soluble tannins of such materials are extremely sensitive to temperature changes, and it would appear that concordance by a rapid-cooling method is only possible under identical conditions of cooling, the longer the time taken for cooling the lower the insolubles and vice versa. Such a method has, however, the advantage of shortening the time of analysis when used in conjunction with a rapid-chroming method, which the International method is, and since 50 cc. are evaporated and a vacuum dryer used, an analysis may be completed within a day. Frequently this is of no inconsiderable moment.

Other methods of estimating tannin are those of Jean, with a solution of iodine in presence of sodium bicarbonate; the "Parker-Payne method," by estimation of the total acidity of a tan solution with standard calcium hydrate, detannization with "collin" (a mixture of gelatine and gelatine-peptones), estimation of the acidity of the detannized solution with the standard calcium hydrate and calculation of the tannin by the difference between the two acidity determinations; Wislicenus, by the aid of "fibroid alumina." I will not go into details of these methods as they have all been proven inferior to the shake method.

I have endeavored in preparing this address to cover as completely as possible all the numerous details of the Official Method, the observance or non-observance of which serve to make or

Digitized by Google

mar the analysis. I cannot impress too strongly upon you the absolute necessity of "obeying the letter of the law "if you desire to attain that concordance which the commercial interests involved demand. It is strange, but nevertheless true, that the leather and tanning extract trades require of the analysis a degree of accuracy, and uniformity of results between analysts, not demanded by many other industries even dealing in inorganic materials. It is not generally recognized that in the analysis of a complex organic substance containing tannin there are difficulties presented that make the concordance actually obtained quite remarkable. It is true that the Official Method of the American Leather Chemists Association is in some particulars open to criticism, not in principle but in detail. The Council of the Association has but recently appointed a committee to revise the wording of the method with the idea of making more intelligible certain obscure points, thereby effecting more exact similarity in procedure in various laboratories. Several of these points I have mentioned.

An address of the nature and on such a subject as you have been listening to is at the best bound to be dry and uninteresting. I trust, however, that you may find it not without value for reference when in the future you have occasion to lock horns with the method of analysis of vegetable tanning materials.

A member of the American Leather Chemists Association must in all public work stamp upon his analysis a certificate to the effect that it was made according to the Official Method of the A. L. C. A. What does it mean if this edict is not obeyed? Leaving aside the ethical question of the integrity of the individual, should an analysis be stamped as officially analyzed when in reality not so, such a departure from the path of honor brings discredit not only upon the method but upon every other individual member of the Association. Whether we are convinced in our own mind that the method is in error has nothing to do with the question, and if we hold such a conviction we should bend our efforts toward alterations in the method to suit such convictions.

In concluding let me request you all, if your future relations are such as to make it possible, to support the American Leather Chemists Association to the best of your ability, and by sup-

Digitized by Google

porting the Association you will support its methods of analysis. The amount of work done by the Association as a whole, and its members individually, to perfect methods is really surprising when one considers how much personal sacrifice has been necessary to accomplish the results attained. It is even more surprising, when one considers the trade interests involved, that commercialism has had no part in framing the methods to the advantage of one and the disadvantage of another. Rather has a spirit of fairness,—unquestionably due to professional discrimination of the merits of the questions arising,—prevailed, to the exclusion of selfish considerations of personal benefit.

Finally, I would express my thanks for your forbearance in giving your attention to so tedious an address, and extend a very cordial invitation to each and every one of you to visit me at the laboratory, whether socially or in search of information upon the problems connected with the analysis of vegetable tanning materials.

TANNING SCHOOL AT LIEGE.

We have received a pamphlet giving the rules of the "Association pour l'Enseignement Professionel de la Tannerie à Liége." This Association was founded in 1898 under the auspices of the "Bourse aux Cuirs de Liége." The pamphlet gives also the courses offered in the school conducted by the Association. Two years' instruction covers courses in general chemistry, leather chemistry, physics, technology of tanning, tanning practice, microscopy and bacteriology, hygiene, and in business and accounts.

The school is under the direction of M. Edouard Nihoul, Sc. D., who is also connected with the University of Liége. He gives the course in leather chemistry. The corps of instruction also includes Joseph Wauters, Sc. D., and Louis Sody, Chemical Engineer.

The course in physics, beside the ordinary subjects, includes detailed study of the machines used in leather making, and of the principles of ventilation, and the testing of fuels. Similarly the course in general chemistry includes special study of the substances used in tanning. The course given by Dr. Nihoul in

Digitized by Google

leather chemistry embraces not only methods of analysis, but a study of all the processes, soaking, liming, picking, bating, tanning and finishing, as well as oil tannage, chrome tannage, etc., from the chemical point of view. The courses in technology and tanning are also very comprehensive.

ABSTRACTS.

New Degreasing Materials, Trichlorethylene and Carbon Tetrachloride. W. EITNER. *Der Gerber*, No. 904, May 1, 1912. Failure to remove grease makes tannage more difficult and reduces the value of the leather. The kinds of skins for which degreasing is most important are sheep, goat and pig. Various methods are successful, some of which remove the grease before and some after tannage. Since fat hinders tannage, it is better to remove it first. The other plan is more common, however, especially with sheepskins, which are harder to degrease in pelt, on account of the kind of fat which they contain. This closely resembles wool-grease, being almost all unsaponifiable. Pigskin contains much fat, but this is saponifiable. The average fat content of different skins varies very much, those of cattle having 0.5 per cent. and pigskin 3 per cent., while sheepskins from some sources have as high as 40 per cent. grease, estimated on the dry weight. Degreasing may be done mechanically, by pressure. This method is adapted to wet untanned skins. Sheepskins are soaked in warm water and then squeezed in a hydraulic press. Although this process does not take out all the fat, it prepares the skins for tannage with sumac or bark liquors. A method much used for Argentine sheepskins drums them (after being unwooled by the sweat process) in a mixture of benzine and methyl alcohol for 1-1½ hours, when they are taken out and pressed. The fat is separated by distillation, involving a loss of 35-40 per cent. of the solvent. This process may also be used with limed sheepskins. Dry leather may also be degreased in a somewhat similar way, East Indian sheep and goat leathers being often thus treated. The apparatus is either of the Soxhlet or the revolving cylinder type. Benzine has been the solvent, or sometimes, especially in France, chloroform. Carbon tetrachloride (CCl_4) and trichlorethylene (C_2HCl_3) are coming into use. They are not dangerous like benzine because they do not burn, nor do they like chloroform produce insensibility when inhaled. CCl_4 has a specific gravity of 1.6, boils at 77° C. (171° F.), and costs in Vienna about 13 cents per pound. C_2HCl_3 has a specific gravity of 1.47, boils at 88° C. (192° F.), and costs in Vienna about 9 cents per pound. A mixture of C_2HCl_3 with a soap is sold under the name trisapon, and this may be used with luke warm water in a drum for degreasing wet hide. The grease is then recovered from the wash water by precipitation with hydrochloric acid. L. B.

Digitized by Google

Restoration of Dry Hides and Skins by the Formic-Mercury Process. ALFRED SEYMOUR-JONES. *Leather World,* IV, 344. A pit for the purpose may be rendered tight by painting. To 20,000 pounds water add 40 pounds 90 per cent. formic acid. After stirring, throw in as many dry hides or skins as the water will cover. Leave them in 24 hours. Draw out and pile on a slope so they will drain into the vat. Put them back for another 24 hours. If they are not now thoroughly softened, they may be immersed another 24 hours. Then salt by laying in a pit with salt or drumming with salt for 15 minutes. The formic acid solution may be strengthened and used over until too dirty to use, or the dirt may be strained out. If the water is hard, this should be neutralized with sulphuric or hydrochloric acid, or the water should be put through a softening process. The loss of hide substance by this process is very small. If sterilization is to be effected, 4 pounds of mercuric chloride are added to the 20,000 pounds of water. L. B.

Manufacture of Matt Chrome Leather. *Gerber-Courier,* Vol. 53, No. 12. Matt chrome leather, since it forms an excellent equivalent for waxed leathers, is rapidly gaining in popularity. Softness and flexibility are desired for this leather and also a certain plumpness, without which it would have a weak loose texture and a coarse refractory grain. Green or fresh salted hides are the best to use since old salted hides become too loose in the soaks, etc., and dry salted hides require too careful a treatment. It is recommended to use sodium sulphide or arsenic in the liming and after the hair is easily removed, to bring the hides a second day in a fresh lime where they are plumped and purified. Lactic acid is best for deliming.

The single bath process for tanning appears to be most suited for this kind of leather. It is best to begin with a weak solution and to strengthen as tanning proceeds. The fat-liquoring of this leather is very important as an excess causes a greasy flabby feeling in the leather. A solution of Marseilles soap and bone oil can be added to the customary fat-liquor. It is advantageous to warm the fat-liquor before using and no danger to the leather need be feared under a temperature of 122° F. to 180° F. Besides the fat-liquor a stuffing of flour, egg-yolk and alum solution may be used for filling and making flexible this leather and tends to give it the feeling and richness so well liked in glazed and kid leathers. After drying, the leather is moistened uniformly and is then flattened or stretched and nailed on a frame to dry again before the finishing. This has been found advantageous as the wrinkles and unevenness are removed and the leather lies smooth and level when dried.

After trimming, a polish is given. A good solution is made from 1½ gallons of water, 1 pound gum, ½ pound yellow wax, ¾ pound Marseilles soap, ½ pound tallow, and about ½ gallon of black coloring composed of concentrated logwood decoction. This is rubbed on uniformily with a piece of flannel. After about ½ hour this has soaked in and the leather

Digitized by Google

may be ironed. Directly after the ironing the leather is given a second polishing. This operation is one of the most important as to it is due the matt lustre similar to kid which characterizes this leather.

L. A. C.

Plumping of Sole-Leather in Northern Germany. *Gerber-Courier,* Vol. 53, No. 15. Plumping by acid liquors in which the acid is formed directly in the process is considered the safest and best means. Boiling of oak bark liquor prevents acid formation. In many tanneries the custom prevails of pouring "Eisenschwarze" into the handlers. This increases the plumping power of the liquor, especially when made fresh from vinegar or sour beer. Recently, however, plumping has been done to a great extent by yeast, acidulated ground barley and wheat bran. Mineral acids, including boric, hydrochloric, pyroligneous and sulphuric are much used, especially the last, where the natural acids of the liquor are not sufficient. The coloring vats are now constructed of stone and cement fitted with galvanized iron bars and hooks upon which the hides are hung. By making a small slit in the extreme part of the hind foot for slipping over the hook, the hides can be made to spread out well and to hang uniformly exposed to the liquor.

The plumping liquor is made from extract liquor by diluting with water and adding one and a half to two bucketsfull of sulphuric or other acid per coloring vat. The vats are filled so that when the hides are hung in, the liquor will be even with the edge of the vat and after thorough plunging are ready for the hides. After the hides are placed in the vats they are withdrawn several times during the day and after 24 hours the plumping and coloring are considered satisfactory. By making a small cut in the hide the action of the acid and liquor can be gauged. Plumping liquor, once used, sould be thrown away but may be strengthened up by the addition of a small quantity of extract liquor diluted with water and a proportional quantity of acid. Hides should be plumped so they will not fall again in the following treatment as such hides do not absorb sufficient tanning material and thus produce a flatter leather.

L. A. C.

Practical Questions from the Chemistry of the Tanstuffs. G. POWARNIN. *Collegium,* 1912, 105-115. The author begins with the following fundamental principles from his book "Probleme aus der Chemie der Gerbstoffe," soon to appear.

(1) Only two chemical reactions characterize the tannins: (a) precipitation by albumen and gelatine (b) by neutral Pb acetate.

(2) The tanstuffs (tannides) are divided into (a) Estero-tannides, containing the group CO.O which can be ruptured at the O union. (b) Kotannides which contain carbon union between the single rings and are obtained by condensation, especially in presence of phloroglucin groups. The esterotannides include a portion of the gallotannides, the

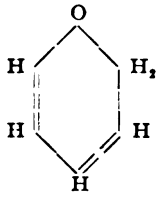
Digitized by Google

kotannides include nearly all the catecholtannides and the rest of the gallotannides. Esterotannides do not give phlobaphenes by dehydration but only on oxidation. Phlobaphenes are generally, although not always, more complicated kotannides.

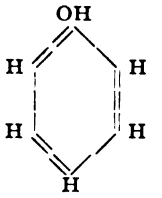
(3) Probably all tannides occur in plants as glucosides (tannosides) but some may quickly split up by fermentation.

(4) Phlobaphenes result mostly by anhydrization, more rarely by oxidation.

(5) All tannins as phenols may exist in solution in two tautomeric forms:



I. Keto form.



II. Enol form.

The keto form predominates in solids and concentrated colloidal solution, also is most marked in large molecules. Most chemical reactions of ketones are given and gelatin is precipitated. The enol form gives phenol reactions, precipitates Pb acetate and is characterized by crystalloidal, dilute solutions. Phlobaphenes incline to the keto form.

(6) The kotannides contain frequently heterocyclic groups, furan, pyron, etc.

A. *Esterotannides.*—Galls, sumac, Coriaria myrtifolia, Lentiscus, knoppern.

B. *Kotannides.*—1. Gallokotannides: myrobalans, algarobilla, divi-divi, valonia, chestnut wood, oak wood. 2. Phlorokotannides; catechu and gambier, kino, quebracho, maletto, birch. 3. Protocatechutannides: pine, hemlock, barbatimao, mangrove, canaigre. 4. Gallotannides: mimosa, Acacia arabica.

Technology of Extraction.—Concentrated solutions contain more phlobaphenes and are colloidal in character; the dilute solutions are more crystalloid. If the plants contain no hydrolytic ferments, the tannosides go unchanged into the liquors; such extracts are found in lay-away vats. The liquors from hot extraction contain more colloids and less tannosides than cold extraction liquors, and resist hydrolysis. In extraction with water containing bicarbonates of Ca or Mg, esterotannides are decomposed forming insoluble tannates. In general, the esterotannides are dissociated by heat while the kotannides give phlobaphenes and the soluble tans are diminished; frequently oxidation promotes the change. Heat also splits off glucose, also lowering tanstuffs. Nihoul has found that water may decompose furan and pyron rings. In extraction with free SO_2 or bisulphites, the author regards the chief action due to a

Digitized by Google

change of the keto form phlobaphenes into double sulphite compounds, R:O yielding R(OH).OS:O(OH) or R(OH).OS:O(ONa). These compounds are unstable but more crystalloid than the original phlobaphenes. In employing soda for extraction, the enol form gives tannate, unfavorable to tannage, but the phlobaphenes are dissolved.

Clarification of Extracts.—The chief object is to remove the dark colored phlobaphenes; these occur in plants containing kotannides (anhydrophlobaphenes). Another problem of lesser importance is the removal of the yellow dyes of the flavon and xanthon type; these accompany esterotannides. The numerous processes are classed:

A. Removal of phlobaphenes without reduction or oxidation. I. Employment of various agents, albumen, gelatin, starch, boneblack, $Al(OH)_3$, which precipitate the phlobaphenes depending upon their colloidal character and high molecular weight; some of the tannin is carried down at the same time and lost. Acids used for this purpose dehydrate the tanstuffs, producing more phlobaphenes hence are ill suited. II. Conversion of the ketophlobaphenes into the enol form: (a) precipitation as insoluble tannates by Zn and Pb salts, alkaline earths, Ca borate, chromo salts; part of the tannin is also here carried down with the phlobaphenes; (b) solution of the phlobaphenes in bases. This is more an adulteration than a purification, for the tannates have no tanning action.

Moron (1886) used soda and casein, Simon & Co. (1892) blood and soda, David (1892) and Pollak & Jurenko (1909) bases.

B. Reduction methods: (a) with sulphites, hyposulphites, hypophosphites. The solvent action of SO_2 has been explained above (extraction). The reducing action has been little studied. Nierenstein has shown that digallic acid goes over into leuco-digallic acid by reduction of the carbonyl of the ester, and this theory can be applied to all the esterotannides. In the kotannides a similar reduction of linking keto or lacton groups may be assumed. Procter has shown that SO_2 also reduces the yellow flavon and xanthon groups. The advantages of this superior process lie in the bleaching of phlobaphenes without loss of tanstuff but rather a slight gain through solution of phlobaphenes; the presence of SO_2 prevents oxidation of the leucotannides. The sulphite addition compounds are active in tanning, being decomposed by the hide. The disadvantages are the formation of free H_2SO_4 through oxidation of SO_2, and the normal weak acid reaction of the extract is a disturbing element, especially with soft leathers.

C. Clarification by oxidation with bichromate entails loss of tannin and has therefore little merit.

Alteration of Extracts.—On storage, with time the insoluble phlobaphenes increase because of anhydrization of kotannides; heat accelerates the decomposition. Sulphited extracts change less. Another change with time is due to hydrolysis of tans by action of micro-organisms and oxygen from the air; the author accepts this view for esterotannides and tannosides, but the hydrolysis of kotannides by ferments would be slow.

Digitized by Google

Analysis of Tanstuffs.—A purely chemical method, based on factors, is scarcely conceivable. The subject of tannosides is important and a method for the determination of tannins before and after fermentation would be useful. The tannosides have less tanning power, the phenol groups being fixed by the glucose radical.

Technology of Tanning.—In vegetable tannage, the keto form of the tanstuff combines with the collagen, while the enol form is incapable of tannage. The crystalloid enol penetrates the hide easiest; therefore sulphited or cold extracts and tannates penetrate well. The conversion of the enol form—$CH=C(OH)$—into the keto form—CH_2-CO—is reversible, proceeding slowly and under conditions not investigated. Acids promote the change while alkalies determine the non-tanning enol form. In normal tannage then, the tanstuff should penetrate the hide in the enol form and thus uniformly divided gradually pass into the keto form, probably by influence of the hide substance. Uniformity in tannage is the most important element. Solidity of leather is not proportional to the tannage, on the contrary tanning weakens the fiber. A certain optimum should not be exceeded, since the resistance to decay is not further increased and the solidity of the leather is diminished. Local irregularity in tannage lowers the total strength. In general, a uniform tannage cannot be secured in a rapid process.

De-tannage by hot water or acids results from decomposition of the collagen tannates. Bases perhaps change the keto to the enol form. After the enol has been absorbed by the hide, the conversion into the keto form progresses with the removal of water. Drying leather promotes and terminates the tanning process and the more gradually and uniformly this proceeds, the better. Over-heating causes oxidation and anhydrization of the tanstuff, darkening the leather. W. J. K.

The Employment of Coal Tar Dyes for Leather and Furs. GEORG GRASSER, *Collegium*, **1912**, 116-121. The substitution of these dyes for the less tractable vegetable colors has in recent times become very successful; they are cheap, of immense yield in color, and uniform and reliable in composition. Vegetable tanned leathers dye the easiest, then follow fat-tanned and glacé leathers; with the last, artificial dyes have overcome the old troubles with dyewood colors. Chrome leather requires the most care. The water used plays an important rôle in all dyeing; chemical control in this direction is advisable. A slight modification in a chrome tanning process can interfere with an established procedure in dyeing, but generally the specially informed tannery chemist can substitute from the great variety offered some other brand of dye producing the desired effect. A list follows of the special leather dyes from the principal manufacturers and their methods of use.

Actiengesellschaft f. Anilin-Fabrication, Berlin.—For vat dyeing, the fells are passed in pairs, flesh to flesh, through three baths of 6 liters per pair (40-60° C.); the average strength is 10 grams dye per liter.

Digitized by Google

The typical dyes for vegetable tanned leather are: aurophosphin, phosphin, leather yellow, brown and black, methylene blue, cotton blue, methyl violet. Drum dyeing is suited for large scale practice: 50-100 fells can be dyed at once in one hour. Brush dyeing is used for leather with undyed flesh; the color is applied at 50° C. in two or three coats. Chrome tanned leather must first be free from acids or alkalies. If a firm grain is to be secured by a fore-treatment with sumac, the basic dyes above named are used. Acid dyes are suited for all sorts of chrome leather. Ponceau, azo acid yellow, fast brown and blue, nigrosin are chief; the dyeing is at 50-60° C., with addition of H_2SO_4. Substantive dyes are best for straight chrome tanned leather; they require no addition whatever. Brilliant purpurin, chrysophenin, Columbia blue, chrome leather black are the most used. The drum best suits chrome leather, the dyes being gradually applied through the axis. Tawed leather is often grounded with vegetable colors and finished with acid dyes. Chamois requires addition of Glauber salt for basic dyes, together with tartar emetic for acid colors.

Similar lists are given for some 12 other manufacturers. Lepetit, Dollfus & Gansser of Milan make so-called chromo-chrome dye-tanstuffs which tan and dye in one operation; black, yellow, orange, brown, red and blue are furnished and can be shaded by other dyes.

Fur dyeing is briefly discussed. W. J. K.

Applied Chemistry in the Service of Tanning. E. STIASNY. *Gerber*, 1912 [38], 101-2. Before the introduction of chrome tannage, scientific investigation contributed little of direct practical use to the tanner. Here chemical control becomes indispensable. The chemist can aid in vegetable tannage by controlling or reproducing the favorable conditions established by pure empiricism. Examples are the proper acidity of liquors or a nitrogen determination in a sample of hide which much more accurately shows the degree of tannage, than the inspection of a section. In chrome tanning, the chemist not only controls but directs. For example, in the preparation of the single bath liquors, the degree of basicity is of great importance. The chemist can determine any desired basicity by the formula $Cr:SO_4 = 52:X$, where X may have any value from 144 (chrome alum) down to 50 when the basic salt ceases to be soluble. For example to prepare a liquor of basicity 52:90, to 1,000 kilos chrome alum

$(144 - 90).2.\frac{106}{96} = 118.8$ kilos calcined soda must be used.

Although the relations are more complicated in the double bath, investigation has shown three principal reactions to prevail. The antichlor is oxidized either completely to sulphate, to tetrathionate, or to sulphate with separation of sulphur. The amount of sulphur separation is comparatively slight and is mostly overlooked because of the formation of a colloidal sulphur solution and secondary union with tetrathionate producing pentathionate. Therefore nearly all the sulphur resulting from

Digitized by Google

the double bath is not a reduction product but the result of direct action of antichlor on acid or chrome salt. W. J. K.

The Purification of Waste Water from Tanneries. W. APPELIUS. Report of Freiberg Tanning School for 1911-12 through *Ledertechn. Rundschau*, 1912 [4], 105-7, 113-7. In general the same principles apply as in all sewage disposal and the writer first treats the subject in a broad way. There is no single satisfactory method of universal application to all situations. Tannery drainage contains lime, magnesia, salt, sodium sulphide, Al and Cr compounds, arsenic, etc.; of organic matter, albumen or hide substance, hair, wool, tannin, saccharine substances, etc. In some situations the drainage may be delivered direct to the river, relying upon the natural "self" purification in the stream. The chief factor then is rapid dilution, depending upon the speed of the current. Pettenkofer's requirement of a dilution of 15 times has proved much too low. If the sewage is well diluted and not allowed to settle, the solids are mechanically divided by friction and then destroyed by the bacteria in the water, aided by dissolved oxygen. Algae, water plants, fish and sunlight aid.

If the above natural purification be impractical, the sewage liquor must be more or less purified before entering the stream. Ordinarily, mechanical settling or clearing (Klärung) is sufficient. The coarsest materials unsuited for pumping are first strained out and to settle the finer particles the rate of flow is reduced by allowing the water to flow horizontally through basins or vertically through towers. The basins are of such a size as to allow 4-8 hours settling and in such number that the rate of flow is 2-10 mm. per second. Dimensions now used are 45-50 meters long, 5-10 m. broad, 2-3 m. deep; the bottom slopes 1:1.25 to 1.75 to the lowest point where the sludge is pumped out. A disadvantage of the system is that the sludge cannot be removed during the operation but every 6-10 days, the basins must be cut off from action for cleaning. This necessitates 1 or 2 reserve basins. For economy of space towers are substituted, the upward flow being secured by exhausting the air. These have a circular or rectangular section of 15-20 square meters with a funnel shaped base. The flow must be slower than in basins, 1.5-1.8 mm. per second. In the mechanical-chemical settling processes, the settling is accelerated by addition of lime, copperas, ferric alum, Al salts; brown coal, peat, bog muck have been used. The heavy precipitate carries down with it the lighter sewage sludge. An important problem is the disposal of the sludge; it is disposed of as fertilizer, gasified for fuel, etc.

In the mechanical settling method as used especially in tanneries, one form of settling basin that has proved useful consists of a cement walled pit provided with wooden partitions which force the water to traverse a great distance and finally settle; the partitions are removable for cleaning; lime is used as precipitant. In one arrangement described and figured, the water after settling in two large basins, is then precipitated by chemicals in a third mixing chamber, provided with a settling basin.

Digitized by Google

The customary methods of testing the purity of the treated water are discussed, and a bibliography of works on the subject in German is here given. W. J. K.

PATENTS.

Process of Curing Hides. U. S. Patent No. 1,025,401. FRANK P. JAMES, Nashville, Tenn., assignor to Electric Meat Curing Co. of Cleveland, O. Fresh hides are washed and suspended in a salt solution, through which an electric current is passed.

Treating Sewage. English Patent No. 366. S. H. ADAMS, Fulford, Yorkshire.

Leather Board. English Patent No. 491.. W. P. THOMPSON, 6 Lord St., Liverpool. (Hide-Ite Leather Co., Boston, Mass.) Leather scrap is dissolved in caustic alkali and precipitated with a salt of aluminum. The precipitate is mixed with ground leather with or without the addition of a chrome salt.

Method of Treating Leather. U. S. Patent No. 1,025,324. WILLIAM R. SMITH, Buffalo, N. Y., assignor to Buffalo Leather Co., Buffalo, N. Y. Leather is rendered water-proof and non-slipping by immersion in a melted mixture of elaterite and ozocerite.

Digitized by Google

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII JULY, 1912 No. 7

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, } . . . . . Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

ELECTIONS.

ACTIVE

Joseph H. Fenner, Eastville, Marfleet, Hull, England.
Harold Brumwell, Leather Dept., Leeds University, Leeds, England.

ASSOCIATE.

Dr. Otto Rohm, Weiterstadterstrasse 4-6, Darmstadt, Germany.
A. W. Cappon, % Cappon and Bertsch Leather Co., Holland, Mich.

CHANGE OF ADDRESS.

C. B. Kinney to 117 Maryland Ave., Milwaukee, Wis.

Digitized by Google

NOTICE.

The Secretary announces that out of 67 ballots returned, 46 members of the Association have voted *not* to hold the next annual meeting at a time coincident with the meeting of the International Congress of Applied Chemistry, and 21 have voted in favor of holding it at this time.

In view of this fact, the Council will hold a meeting and decide upon the date of the next annual meeting.

H. C. REED,
Secretary.

PRELIMINARY REPORT ON LIGHT LEATHER LIMING CONTROL.[1]

By Joseph T. Wood and Douglas J. Law.

SYNOPSIS. Introduction. Alkalinity of old limes. Filtration. Centrifuging. Indicators. Hydrogen ion concentration of new and old limes. Ammonia. Sulphides.

Dissolved skin substance in old limes. Kjeldahl method. Precipitation method. Stiasny's method. Bennett's method.

Differentiation of products of hydrolysis, Eitner, Stiasny, various salting out methods. Bacteria and their products in limes.

While the use of lime in the preparation of skins for tanning is of great antiquity, the scientific study of the process is of recent date. In Procter's Text-Book of Tanning (*Spon.*, 1885, p. 139) referring to the use of lime he remarks: "The qualities of lime, its virtues and failings, have been matter of experience for hundreds of years, and so far as such experience can teach, we know exactly how to deal with it. A new method, on the other hand, brings new and unlooked for difficulties, and often requires changes in other parts of the process, as well as in the mere unhairing, to make it successful. As our knowledge of the chemical and physical changes involved becomes greater, we may look to overcoming these obstacles more readily; for the power of dealing successfully with new difficulties constitutes one of the main advantages of a really scientific knowledge over an empirical one."

[1] Collegium, No. 504, pp. 121-130.

Digitized by Google

We do not propose to repeat the information contained in the text-books, but to outline a scheme of control, so that its details may be filled in at the Conference of the I. A. L. T. C. to be held in London, 1912, and a new uniform method of working adopted by our members in the same way as for the estimation of tannin.

The swelling action of a pure solution of lime on skin is said to be due to the hydroxyl ions, therefore the first determination to be made is the total alkalinity of the lime liquor. As is well known, saturated lime water at 15° C. contains 1.211 grams CaO per liter, which consumes 433 cc. N/10 acid for its saturation. Limes in use contain also neutral salts of lime; lime in combination with skin substance, sulphides from the hair, and ammonia produced by the action of lime on the skins, they are thus always more alkaline than lime water. Before the liquor is titrated it must be decided whether it shall be filtered or merely allowed to settle, and the supernatant liquid used. The question of filtration has not yet received the attention it deserves since the degree of clearness of the filtered liquor has a great effect on its alkalinity, as the following example will show. The quantity of liquor taken was 10 cc. of a weak, old lime (frizers collecting pit):

Unfiltered liquor required	4.5 cc. N/10 HCl
Filtered through cotton wool.....	4.2 cc. N/10 HCl
Filtered through S. and S. 605 (clear)..	3.2 cc. N/10 HCl

The candle filter was tried, but was found to be useless, owing to the colloidal character of the liquors.

S. and S. 605 filter-paper as used for filtering tan liquors appears to be the only medium which gives a perfectly clear filtrate. Filtered in this way, very few even of the oldest limes have an alkalinity greater than 4.7 cc. N/10 HCl for 10 cc. liquor. The filtration is necessarily extremely slow, and no doubt ammonia is lost by evaporation. To obviate this Trotman (*Leather Trades Chemistry*, p. 63) recommends a special funnel with ground edges fitted with a bell cap, carrying a soda lime tube, and where greater accuracy is required, this is necessary. Professor Stiasny proposes to centrifuge the liquor, and we have

Digitized by Google

made some experiments in this way with the following results, using a four weeks old lime with many pelts through it:

Filtered through cotton wool ..... 17.8 cc. N/10 HCl
Filtered through S. and S. 605..... 5.0 cc. N/10 HCl
Unfiltered centrifuged 5 minutes..... 8.4 cc. N/10 HCl

This was a bad, old lime highly charged with skin substance. The liquor after filtering through cotton wool when centrifuged gave a sediment almost as great as the original liquor. It is therefore evident that filtering through cotton wool does not remove the particles of lime; indeed the centrifuging for 5 minutes only removes particles ranging in size from a little less than 1 μ upwards. After centrifuging, the liquor still contains an enormous number of extremely fine particles 0.5 μ and less in diameter. In addition to the spherical concretions of carbonate of lime mentioned by Procter (*L. I. L. B.*, p. 91) crystals of calcium carbonate, mostly in the form of calcspar, occur; arragonite crystals are also seen. It is mainly these crystals which cause the difference in alkalinity between a filtered and unfiltered lime liquor, although some lime combined with skin substance is also removed by filtration. Centrifuging is better than filtering unless an absolutely clear liquid free from all particles, *i. e.*, optically clear, is required, and this, as we shall show later, removes not only particles of solid matter (lime compounds and bacteria) but also colloidal skin substance.

Stiasny finds that kaolin addition does not give satisfactory results in filtration.

As an indicator we have found methyl red preferable to phenolphthalein which does not estimate the whole of the alkalinity, and has not a very sharp end reaction, owing to the presence of ammonia.

The following are comparative titrations using methyl red and phenolphthalein respectively, as indicators (cc. N/10 HCl for 10 cc. filtered liquor):

Methyl Red	Phenolphthalein
5.5	4.2
6.3	4.5
4.3	3.2
4.2	3.0
4.5	3.3
8.9	6.5

Digitized by Google

As will be seen, the ratio between the figures is not uniform, but is no doubt roughly proportional to the weak bases present in the liquor, which do not affect phenolphthalein. The color change of the latter occurs at a hydrogen ion concentration of 10^{-9} normal, whereas methyl red changes at 10^{-6} to 10^{-7}. The turning point of methyl red is sharper than that of either phenolphthalein or methyl orange.

Hydroxyl Ion Concentration.—We have estimated this by means of the electrometric method, and find the hydrogen ion concentration in old limes practically the same as in new limes. The following results were obtained, using a calomel electrode with N/1 potassium chloride solution, and 3.5 N potassium chloride solution as the connecting liquid.

Lime water 10 cc. required 4.4 cc. N/10 HCl phenolphthalein
4.5 cc. N/10 HCl methyl red

Potential difference = 1.0 volt corresponding to a hydrogen ion concentration (p_H^+) of 12.5.

Old lime required 5.7 cc. N/10 HCl phenolphthalein
6.9 cc. N/10 HCl methyl red

Potential difference = 1.005 volt corresponding to (p_H^+) 12.34.

This liquor frothed almost like a soap solution with the hydrogen; it had no swelling action on the skin.

It would thus appear that the swelling action of the hydroxyl ions is hindered by the presence of various compounds produced both by the action of lime on the skin and also by the action of bacteria on the dissolved skin substance, although these bodies do not affect the hydrogen ion concentration of the liquor.

By using methyl red as indicator, the total alkalinity of the liquor is estimated, this including that due to ammonia and sulphides, if present. While the extra alkalinity of the lime, if due to sulphides, is no indication of the skin dissolving power of the liquor, the method is of advantage, in that the end-point is sharp, which is not the case with the other indicators, and the amount of sulphides and ammonia being found by the other methods the alkalinity actually due to caustic lime is easily calculated by subtraction.

The addition of sodium sulphide has no effect on the hydroxyl ion concentration of a lime liquor, even if it is present in such a quantity as to double the titration figure.

Digitized by Google

AMMONIA.

The methods of Procter and McCandlish (*Collegium*, 1906, p. 270) and of Schloessing, although more accurate than the distillation methods, are unsuitable for works control, on account of the length of time required for the determination. Of the distillation methods, the most satisfactory is that in which calcined magnesia is used to decompose ammonium salts, as suggested by Procter (*L. I. L. B.*, p. 63). The solubility of the alkali is so small that no appreciable hydrolysis of the organic matter takes place during the distillation, and therefore all the ammonia distilled over is derived from actual ammonium salts in the liquor. This being so, it is not necessary that the liquor should be filtered. One hundred cc. of the liquor is placed in a distilling flask with a little methyl-orange, and dilute hydrochloric acid added until the indicator is just reddened. Considerable excess of magnesia is then added, and the ammonia distilled off in the usual way into a measured quantity of standard acid and titrated back. The method, while not being absolutely accurate, is quite sufficiently so for works control purposes. Determinations on the same liquor give very concordant results, but estimations made of known quantities of ammonia added to a lime liquor give results slightly on the low side. Frothing is minimized by adding a few drops of turpentine before distilling, and is less when no additional water has been added to the liquor. Three determinations of ammonia in a lime liquor gave the following results as ammonia in grams per liter:

1	0.2072
2	0.2072
3	0.2044

Some results obtained on adding known amounts of ammonia to an old lime liquor, and estimating the same by the method were as follows:

	NH_3 added grms. per litre	NH_3 found grms. per litre
1	0.3400	0.3374
2	0.1344	0.1330
3	0.1372	0.1302

Digitized by Google

SULPHIDES.

Sulphides are most conveniently estimated by titration with standard zinc sulphate solution (Procter, *L. I. L. B.*, p. 55). Twenty-five cc. of the filtered or centrifuged lime liquor is titrated with a solution of zinc sulphate containing 14.35 grams of crystallized zinc sulphate per liter. Before making up the zinc sulphate solution to one liter ammonia is added until the precipitate formed is just redissolved. A drop of the solution is removed from time to time as the titration proceeds, and placed on a piece of filter paper, so that its edge is in contact with a similar spot of lead acetate solution. The zinc sulphate solution is added until no black or brown color is produced at the point of contact of the rings, when all the sulphides in the liquor will have been precipitated. The soultion of zinc sulphate is decinormal, so that each cc. will correspond to 1.6 milligrams sulphur, or 12 milligrams crystallized sodium sulphide. Traces of sulphide will be found in all old lime liquors, even if none has been added or introduced in the goods, being due to the decomposition by the alkali of the animal matter containing sulphur.

DISSOLVED SKIN SUBSTANCE.

The total nitrogen in all the products of hydrolysis of the skin substance is estimated by the Kjeldahl process. Twenty to 50 cc. of the lime liquor is boiled nearly to dryness after acidification with dilute sulphuric acid, 15 cc. of strong sulphuric acid is added, together with some crystals of potassium sulphate, and boiled well until colorless, when the ammonia is distilled off, and estimated in the usual manner. Under these conditions, the whole process may be completed in about two hours, and there is not much objection to the method on account of length of time. The total nitrogen as found in this way is not necessarily derived all from leather forming material, but much is due to solution of epidermal and interfibrillar matter as has been pointed out by Procter, which must necessarily be removed from the skin. Some of the nitrogenous matter is not completely dissolved in the liquor, and would be removed by a clear filtration, and it is preferable to filter the liquors for Kjeldahl analysis through wool, or better to settle out the grosser particles by centrifuging. The following table shows the increase of nitrogen in a lime

Digitized by Google

liquor used for liming sheep skins, which was analyzed each time the goods were taken out, and also the difference in the nitrogen found made by filtration compared with that found in the centrifuged liquor. It is also seen that a much greater increase of nitrogen is found after the first draw of fresh goods through the pit than that after subsequent draws; part of this nitrogen is due to epidermal matter, etc.

		Limepit 6		
No.	Sample taken Date	(Filtered) N per litre	(Centrifuged) N per litre	Remarks
2301	27/2/11	0.0280	0.0252	No goods been in.
2309	1/3/11	0.2156	0.2156	Goods, which had already been in 2 weaker limes, had been in 24 hrs. then out for 24 hrs.
2319	3/3/11	0.3560	0.3780	Goods, same as 2309, had been back 24 hrs. and then out 24 hrs.
2328	6/3/11	0.4676	0.4900	Same goods back again and out all Sunday (5/3/11).
2346	8/3/11	0.5516	0.5628	Same goods in 24 hrs. and out 24 hrs. These goods were then fully limed.
2352	10/3/11	0.8064	0.8736	New lot of goods in 24 hrs. and out 24 hrs. These goods had already been through 2 limes.
2358	13/3/11	0.9744	1.0472	Same goods in 24 hrs. and out over Sunday (12/3/11).
2367	15/3/11	1.1256	1.2208	Same goods, in 24 hrs. and out 24 hrs.
2380	17/3/11	1.2040	1.2992	Same goods, in 24 hrs. and out 24 hrs. These goods are now finished.
2385	20/3/11	1.6520	1.7430	Green goods, in 24 hrs. and out over Sunday (19/3/11).
2390	21/3/11	1.7150	1.8270	Same goods in another 24 hrs. Pit then run away.

The following are the principal processes which have been suggested as works control methods in addition to the Kjeldahl method:

1. *Precipitation Method.*—Fifty cc. of the filtered lime liquor is placed in a measuring cylinder, a little phenolphthalein added, and acetic acid added till slightly acid; the cylinder is then filled to the 100 cc. mark with saturated salt solution, and the volume of the precipitated hide substance read off after standing for a

Digitized by Google

certain time. The method is extremely rough, but may be used as a comparative test. The amount of acid added has a great effect on the amount of hide substance precipitated. When the solution is made just acid with hydrochloric acid more is precipitated than when acetic acid is used, but with excess of either the amount is about the same with each acid. Very little more is precipitated by saturating the solution with salt than by having the solution half saturated. The volume of precipitated matter as read on the scale lessens very rapidly on standing, as precipitation is very incomplete. In a lime liquor which contains 0.1394 gram of total nitrogen in 50 cc., 0.0671 gram N was precipitated by the acid and salt, showing that about half only of the total nitrogen is thus removed. On further treatment of the precipitate with water:

0.0364 gram was dissolved at 50° C. and
0.0126 gram by boiling water, leaving
0.0181 gram (consisting of Keratin?)

2. *Stiasny's method* (Collegium, 1908, 373-375) consists in titrating the acidity produced by adding neutral formaldehyde to the neutralized lime liquor. If the liquors contain sulphides it is necessary that they should be precipitated before the titration. This was done in the first case by means of zinc sulphate, which led, however, to a slight error through partial precipitation thereby of dissolved hide substance. In a later paper (*Collegium*, 1910, 181-187) the author substitutes the use of iodine solution for the removal of sulphides, and the method is as follows: Fifty cc. of the filtered lime is neutralized with 10 per cent. acetic acid, using phenolphthalein as indicator, and a dilute iodine solution added until a slight excess is present. N/5 caustic soda solution is then added till the phenolphthalein is reddened, and after adding 10 cc. of neutral 40 per cent. formaldehyde solution the titration is carried out with N/5 caustic soda. The author points out that only those amino groups which are connected with carboxyl groups cause an increased acidity of the liquor after adding formaldehyde. The compounds contain different quantities of nitrogen in this form, and also some nitrogen which does not react at all with formaldehyde, and from this Stiasny has shown that a measure of the degree of hydrolysis of the dissolved skin substance may be obtained (see under).

Digitized by Google

3. *Bennett's method*[1] consists in titrating 25 cc. of the filtered liquor with N/10 HCl, using first phenolphthalein as indicator, and then methyl-orange, the difference in the amount of acid required in the two cases being a measure of the dissolved skin substance. The author found a very constant factor connecting this figure with the total nitrogen found by the Kjeldahl method, but the principle of the method is incorrect if sulphides are present, and the constancy of the factor could not be verified by other investigators, nor are the end reactions at all sharp.

DIFFERENTIATION OF HYDROLYTIC PRODUCTS.

1. *Eitner's method* (*Gerber*, 1895, *L. I. L. B.*, 88-89) consisted in precipitating the lime in a measured quantity of the filtered liquor with carbon dioxide, collecting on a tared filter, washing with water and dilute hydrochloric acid, and weighing after drying at 100° C. as "dissolved hide substance in combination with lime." The filtrate was precipitated by acidifying with hydrochloric acid, and the precipitate washed, dried and weighed as "organic substance uncombined with lime." Procter considers the distinction doubtful, as all organic calcium compounds would probably not be decomposed by carbonic acid. The peptones were determined in the filtrate by means of sodium hypochlorite, or by the method of Hallopeau, in which basic mercuric nitrate is used as a precipitant. The precipitate after standing 18-24 hours is collected on a tared filter, washed with cold water, dried at 108° C., and weighed, and two-thirds of its weight reckoned as peptones. Procter states that this method does not include all organic products present, especially the amines, and amido acids.

2. *Trotman and Hackford's method* consists in acidifying the hot filtered lime liquor and saturating with zinc sulphate, which precipitates the albumoses. The peptones in the filtrate are precipitated with tannin, filtered off, and the nitrogen determined in the dry precipitate by Kjeldahl's method, the factor for conversion of nitrogen into peptones being 5.42.

3. *Wood and Trotman's method* used in the examination of "Collin" for the analysis of gelatine, and its decomposition

[1] Described in J. S. C. I. March 31st, 1909, but the principle of the method was published by Stiasny (Der Gerber 1906, 229). See also Collegium 1909, p. 194 and this Journal, Vol. IV, p. 143.

Digitized by Google

products. Unchanged gelatine is precipitated by saturating the solution with zinc sulphate, and estimating the nitrogen in the precipitate. Peptones are precipitated in the filtrate by adding excess of bromine water, and the nitrogen estimated also in this precipitate. The nitrogen found in the filtrate from the bromine precipitate represents amido acids, amines, and ammonia.

The Tannin Precipitation Method (Procter, *L. I. L. B.*, 89).—Twenty-five cc. of a filtered lime liquor was made faintly acid with acetic acid, and excess of tannin solution added, the precipitate was filtered off, and the nitrogen in it determined by Kjeldahl's method. The nitrogen in 25 cc. of the original filtered liquor amounted to 0.0326 gram, while that in the precipitate was 0.0221 gram. Thus in the liquor containing 1.3048 grams of nitrogen per liter the amount precipitable by tannin was 0.8848 gram per liter, or 67.8 per cent. of the total nitrogen. This percentage is, as might have been expected, of the same order as that of the alcohol preccipitable substances, but somewhat higher. The determination of the tannin precipitable matter is certainly of value as indicating what proportion of the dissolved nitrogenous matter would, if left in the skin, have been transformed into leather.

Information which might be of value is attained by precipitating the filtered and neutralized liquor with alcohol. To 25 cc. of a filtered lime liquor containing 0.840 gram N per liter N/1 HCl was added until neutral to phenolphthalein and 50 cc. of alcohol. The precipitate was filtered on a tared filter, washed with alcohol, and weighed after drying at 100° C. The precipitate weighed 1.01 grams and contained 13.0 per cent. N. The nitrogen precipitated in this way therefore amounted to 0.543 gram per liter, *i. e.*, 64.6 per cent. of the total nitrogen. The amount of organic matter precipitated in this way is practically all that is precipitable by alcohol of any strength, and represents presumably all the organic matter above a certain degree of hydrolysis.

Stiasny's method (*Collegium*, 1910, 181-187; Abstr., this J., V, 345) consists in the comparison of the total nitrogen as found by Kjeldahl's method with the formaldehyde titration figure. By means of this an approximate idea of the extent of the hydrolysis

Digitized by Google

undergone by the dissolved skin substance may be obtained, as the factor connecting the total nitrogen with the titration figure after the addition of formaldehyde becomes less as hydrolysis proceeds. The factor expressing the degree of hydrolysis is given by the formula N/C, where N equals the number of milligrams of nitrogen found in a certain volume of the liquor, and C the number of cc. of N/5 soda required to neutralize the same volume of liquor after the addition of formaldehyde to the neutral liquor:

Hydrolyzed gelatine	1 cc. N/5 NaOH =	5.9 mgm. N
Witte Peptone hydrolyzed	1 cc. N/5 NaOH =	7.2 mgm. N
Glycocoll monamino acids ammonia	1 cc. N/5 NaOH =	2.8 mgm. N
Diamino acids—		
Lysin	1 cc. N/5 NaOH =	5.6 mgm. N
Arginin	1 cc. N/5 NaOH =	11.2 mgm. N
Histidin	1 cc. N/5 NaOH =	8.4 mgm. N

At the present stage of our knowledge with regard to the dissolved hide substance in lime liquors, it seems that the two figures, (1) the total nitrogen by Kjeldahl's method, and (2) the factor by Stiasny's formaldehyde method, will give all the information that can readily be obtained. For the sake of simplicity, the factor found by Stiasny for gelatine (178) might be taken as 0, *i. e.*, there is no hydrolysis beyond that required to bring hide substance into solution. If the factor for the final hydrolysis compound (ammonium salts 2.8) then be taken as 100, any intermediate factor between these two may be calculated to express percentage hydrolysis undergone. If, for example, the factor $\frac{\text{mgm. N}}{\text{cc N/5 soda}}$ for a lime liquor came to 12, the percentage hydrolysis in the liquor would be $100 - \left[(12 - 2.8) \times \frac{100}{175.2}\right] = 94.8$ per cent.

BACTERIA AND THEIR PRODUCTS IN THE LIMES.

An old lime in which pelts had been worked 3-4 weeks was examined under the microscope with $^1/_{12}$ o. i. objective and Swift's dark ground condenser with 500 c. p. Nernst lamp illumination. The field was full of brilliant particles all in motion. A large number of bacteria in pairs were seen; owing to the Brownian movement it was difficult to distinguish between inert particles and micrococci, except in the case of crystals. The particles vary in size from 1.5 μ downwards. Numerous crystals

Digitized by Google

of calcium carbonate and possibly other salts of calcium are seen, forming very beautiful microscopic objects.

A single loop of this lime inoculated into ordinary nutrient gelatine, to which a drop or two of ammonia was added, developed about 50 colonies, the estimated number of bacteria per cc. of lime liquor being about 50,000. This is a very low number, and there were undoubtedly many more organisms present, although they failed to come to development in the nutrient medium used. In the soaks there are approximately 1,000 times as many bacteria.

The principal colonies developing were small, round, yellowish ones, granular under a low power. They consisted of small bacteria in pairs, diplococci one of three cells not motile except for the Brownian movement. There were also a number of colonies of a pinkish color, the bacteria of which resembled B. prodigiosus.

Some of the yellow colonies were surrounded by a ring of liquefied gelatine and corresponded with Micrococcus flavus liquefaciens, the non-liquefying colonies being probably identical with Micrococcus Aurantiacus. The yellowish color of old limes is possible due to these bacteria.

There were also some fluorescent greyish colonies forming apparently swarming islets like Proteus Vulgaris, but these again were cocci, and not identical with Hauser's bacillus.

The exact mode of action of the bacteria has not been investigated, but it is no doubt somewhat as follows: fresh lime dissolves the interfibrillar substance of the skin. Bacteria from the air develop in this medium, and decompose the dissolved skin substance by means of various enzymes into gelatones (gelatine-peptones). These are then broken down, further (hydrolyzed) into amino-acids, and eventually into simpler bodies such as ammonia, caproic acid, etc.

The number of species of bacteria capable of developing in a lime liquor is limited by its alkalinity. The bacteria found on the roots of wool removed in a "sweating stove" are capable of growing in a liquid as alkaline as $^1/_{20}$ normal or more, and when grown in nutrient peptonized gelatine produce a considerable quantity of ammonia. Very similar bacteria are found in the

Digitized by Google

limes, and as has been pointed out by Wood (*J. S. C. I.*, 1910, p. 667; this J., V, 360-83) it is highly probable that the unhairing action in both limes and "sweating stove" is due to the same bacteria, not necessarily a single species.

The growth of bacteria in limes is the principal factor producing the "mellowing" of the lime. Griffith (*J. Amer. Leath. Chem. Ass.*, 1910, 109-129) states that the mellowness of a used lime liquor may be artificially produced by the addition of ammonium sulphate.

THE ESTIMATION OF SULPHIDES IN LIME LIQUORS.[1]

By J. R. Blockley, M.Sc., and P. V. Mehd, M.A., B.Sc.

The objects of the experiments recorded in this paper were threefold. (1) To devise a rapid and sufficiently exact method for the estimation of sulphides in lime liquors. (2) To determine, if possible, what is the mechanism of the reactions by which the epidermis is dissolved and the hair rendered loose. (3) To determine what the differences are between lime and sulphide pastes made in the different ways which are used in practice.

Method of estimating sulphides in lime liquors.—Several attempts were made to obtain a rapid method for the estimation of small quantities of sulphides in lime liquors. One method, which seemed promising at first but which was found to fail in certain respects, was a colorimetric method, based on matching the color obtained with a solution of sodium nitroprusside and a standard solution of sodium sulphide, similar to the colorimetric method for the estimation of small quantities of iron.

The method which was finally adopted as being the most reliable was a volumetric method, using a solution of zinc sulphate. Zinc sulphate alone cannot be used to determine the amount of sulphide in a liquor containing lime or caustic alkali, because the zinc is precipitated not only as sulphide but also as hydroxide. If, however, the zinc sulphate solution contains an excess of ammonium chloride, the precipitation of hydroxide is prevented, and the only precipitate is, therefore, zinc sulphide and the ordi-

[1] *J. Soc. Chem. Ind.*, XXXI, 369-71, April 30, 1912.

Digitized by Google

nary end point with lead acetate or sodium nitroprusside can be obtained with accuracy.

Procter states (Leather Industries Laboratory Book, pp. 55, 87) that sulphides in lime liquors can be estimated by a zinc sulphate solution made by dissolving in water and adding ammonia until the precipitate just redissolves. We find that this gives abnormal results, due to the precipitate of zinc as hydroxide. This solution can be used, however, if an excess of ammonium chloride be added to the liquor to be titrated.

For the estimation of the sulphides in lime liquor, a $N/10$ solution of zinc sulphate, to which has been added 50 grams per liter of ammonium chloride, is used. With the concentrations of the liquors in use in practice, it was found that sodium nitroprusside as external indicator gave better results than lead acetate.

The following table shows what sort of accuracy may be expected by the method, and what the error is if zinc sulphate solution, prepared by adding ammonia until the precipitate just redissolves, is used.

Solution	Titrated with N/10 zinc sulphate made alkaline with ammonia	Error per cent.	Titrated with N/10 zinc sulphate to which has been added 50 grs. per l. of ammonium chloride	Error per cent.
Sodium sulphide 0.2%.....	0.2	0	0.2	0
Saturated lime water + 0.2% sodium sulphide	0.23	14	0.2	0
Saturated lime water + 0.1% sodium sulphide	0.118	18	0.103	3
Saturated lime water + 0.05% sodium sulphide	0.066	32	0.051	2

When using a sulphide lime liquor in the yard, it is often of advantage to be able to use it over again, and it is sometimes difficult to know how much sodium sulphide to add to bring it to the original strength. By a simple titration therefore in this way, it is possible to strengthen up again to the desired extent.

Alkalinity of lime liquors containing sulphide.—The alkalinity of a lime liquor furnishes valuable information with regard to the age or mellowness of the liquor. A fresh pure lime liquor has an almost constant alkalinity, being merely that of a saturated solution of lime. As the hides pass through the liquor, some of

Digitized by Google

the nitrogenous organic matter of the hides is decomposed and split up into soluble amino compounds, which thereby increase the alkalinity of the solution. In this way the alkalinity gives an indication of the age of the liquor, and is often taken as a guide to the condition of the liquor, and in practice it is common to use the liquors until a certain alkalinity is reached and then run them down the drain.

This measurement of alkalinity is not applicable in the presence of sodium sulphide, because of the additional alkalinity given by the sodium sulphide, and therefore the alkalinity of a sulphide liquor gives no indication of the age or mellowness, unless account be taken of the amount of sulphide.

If, however, the amount of sulphide be determined and the alkalinity corresponding to it, be subtracted from the total alkalinity, the resulting alkalinity is no criterion as to the mellowness of the liquor, as might be expected to be the case. This arises from the fact that the addition of sodium sulphide to a saturated lime liquor, throws out of solution some of the lime. The addition of hydroxyl ions from the sodium sulphide increases the solubility product and causes the precipitation of some calcium hydroxide similar to the precipitation of sodium chloride from a saturated solution, by the addition of hydrochloric acid.

The alkalinity, therefore, of a sulphide lime liquor does not correspond to the sum of the alkalinities of the lime and the sulphide, and a sulphide lime liquor contains less lime than a pure lime liquor.

The following figures show how the total alkalinity varies as the amount of sodium sulphide increases. (The alkalinity was determined with methyl orange as indicator, phenolphthalein only indicates half the sulphide.)

Solution	Total alkalinity of 100 c.c.s. N/10 hydrochloric acid methyl orange	Alkalinity due to lime
Saturated lime liquor	44.0	44.0
Saturated lime liquor + N/10 sodium sulphide	136.2	36.2
Saturated lime liquor + N/5 sodium sulphide	225.0	25.0

Reactions between lime and sodium sulphide.—The reactions which may take place when sodium sulphide is added to a lime liquor are numerous, and it is not easy to say which compounds

Digitized by Google

are the effective ones in loosing the hair. If a piece of skin be placed in a fresh lime liquor or in a solution of sodium sulphide in water, the loosening of the hair takes place very slowly, but when the skin is placed in a solution containing both lime and sulphide the hair is loosened very quickly. The active unhairing agent is therefore not lime or sodium sulphide. Stiasny has shown (Der Gerber, 1906, Abstr. this Journal II, 55) that when lime and arsenic sulphide are used together for depilation, the active agents are calcium sulphydrates. Experiments were therefore undertaken to determine what the active constituents are in mixtures of sodium sulphide and lime.

Two series of experiments were carried out, the first to determine what is formed when sodium sulphide and lime are mixed in various ways, and the second to determine what changes take place in a sulphide lime liquor when pieces of hide are placed in.

Reactions between lime and sodium sulphide.—To determine what the compounds are which are formed when sodium sulphide and lime are mixed together, the following plan was adopted.

When sodium sulphide and lime are mixed the following compounds might be formed or present: sodium sulphide, sulphydrate and hydroxide, calcium hydroxide, sulphide, sulphydrate, hydroxysulphydrate, or polysulphides. Of these compounds, the sodium salts and calcium sulphydrate, sulphide, and polysulphides are soluble in absolute alcohol; the others are insoluble. Pastes of lime and sodium sulphide were made with as little water as possible, and then extracted with absolute alcohol, and the solution so obtained analysed for the amount of sulphur present and for the amount of calcium present.

With pastes made with the proportions of sodium sulphide and lime which are commonly used in practice, there was no calcium salt present in the alcohol extraction. This excludes, therefore, calcium sulphide, sulphydrate, and polysulphides as the active principle; since these are not formed, the only other compounds are calcium hydroxide and hydroxy-sulphydrate and the sodium compounds. Of these the latter is the only one possible, since the sodium compounds are all present in a pure sodium sulphide solution when no unhairing takes place, and the calcium hydroxide alone has no action.

Digitized by Google

The calcium hydroxysulphydrate is probably formed in some such way as the following:—

$$Ca(OH)_2 + Na_2S + H_2O = Ca(SH)(OH) + 2NaOH.$$

The resulting compounds therefore will be sodium hydroxide, sulphydrate and calcium hydroxide, and hydroxysulphydrate. This applies to the pastes which are used in practice in which the proportion of sodium sulphide to lime does not reach higher than one of sulphide to two of lime. (In practice the proportion of sulphide to lime is much less than this.)

Having determined what compounds are possible, it was attempted to determine to what extent these compounds are formed. The amount of sulphur in the alcohol extraction gives a measure of this extent. The only sulphur compounds soluble in alcohol are the sodium compounds, and therefore the original amount of sulphur minus the amount of sulphur present in the alcohol extraction, gives the amount of the $Ca(SH)(OH)$ compound which is formed. With the mixtures which were taken in these experiments, nearly one-half of the sodium sulphide was reacted upon to form the calcium hydroxysulphydrate. It remains to be proved whether under different conditions of mixing the sulphide and the lime, different results are obtained, and experiments are now being made to determine what differences there are in the lime and sulphide pastes prepared in different ways.

In practice it is usually thought better to mix the unslaked lime and the sodium sulphide together, and add water to the mixture, rather than to add a solution of sodium sulphide to already slaked lime. So far the experiments have shown no difference in the results.

That the reaction between the lime and the sulphide is to form calcium hydroxysulphydrate, confirmatory evidence was given by the fact that the total alkalinity of the alcohol extractions, just corresponded to he total amount of sodium compounds, and this is in accordance with the above reaction.

One point in connection with the mixing of lime and sodium sulphide is the production of a green color. This green color is due to traces of iron, and it was found exceedingly difficult to obtain lime free from iron. The green color is much more accentuated when the sulphide and lime are slaked together, than

Digitized by Google

when the two are dissolved separately and mixed. In fact, quite a large amount of iron may be present before a green color is obtained, when the two are dissolved separately and mixed, whereas the merest trace of iron will be revealed if they are slaked together.

In comparative experiments on the length of time required to loosen the wool from sheepskins, using pastes made up in these two different ways, there was no apparent difference, neither was any difference found in the amount of calcium hydroxysulphydrate which was formed.

The above experiments could only be carried out on lime and sulphide pastes such as are used by fellmongers for removing the wool from sheepskins. It was impossible to determine if the same sort of result obtains, in the weak sulphide liquors which are used for unhairing heavy hides.

Experiments on the absorption of alkali by pelt in lime liquors containing sulphides.—To determine, if possible, what changes take place when hides are placed in lime liquors containing sulphide, experiments were carried out by suspending pieces of hide in liquors made in different ways, and estimating the total alkalinity and the sulphur content of the liquor from time to time.

Pieces of washed soaked hides were placed in the following liquors: *A.* milk of lime; *B.* $N/20$ sodium sulphide; C. milk of lime + $N/20$ sodium sulphide. The last one represents the sort of sulphide liquor which is used in practice for heavy hides.

The following table shows the alkalinity of 100 cc. of the liquor using $N/10$ hydrochloric acid:—

		Originally	After 24 hrs.	After 72 hrs.	After 120 hrs.	After 192 hrs.
A.	Phenolphthalein	44.0	42	42	44	46
	Methyl orange	44.1	43	44	48	52
	Difference	0.1	1	2	4	6
B.	Phenolphthalein	26.0	10	8	9	9
	Methyl orange	49.5	32	30	31	34
	Difference	23.5	22	22	22	25
C.	Phenolphthalein	59.2	55	58	62	64
	Methyl orange	83.6	75	85	88	95
	Difference	24.4	20	27	26	31

Digitized by Google

It will bee seen that alkalinity of the milk of lime very slowly increases. The alkalinity of the soda sulphide alone, diminishes at first very rapidly and then increases again, but it is only the alkalinity with phenolphthalein which diminishes at all. This seems to point to the fact that sodium hydroxide is absorbed very rapidly at first, and that sodium sulphydrate or sulphide is only very slowly absorbed; this is confirmed by the sulphur determinations.

The increase in alkalinity is due to the decomposition products of the hide, namely, the amino compounds.

With the mixture of sulphide and lime the alkalinity decreases rapidly at first, and then begins to increase slowly, and finally increases very rapidly. The very rapid increase of alkalinity shows the vigorous action of the mixture as compared with the action of the lime and sulphide alone. It appears as though the sodium hydroxide is rapidly absorbed, and that the sulphur compounds are only slowly absorbed. This is confirmed by the sulphur determinations, which were as follows:—

	Originally 100 c.c.s. N/10 zinc sulphate	After 24 hrs.	After 72 hrs.	After 120 hrs.	After 192 hrs.
B.	49.5	45	34	27	22
C.	49.0	40	33	30	20

The hair was loose in *C* in two days, in *B* in five or six days, and not at all in *A*.

Amount of hide substance lost.—Determinations of dissolved hide substance were also made in the above liquors from time to time. At the end of eight days the amounts of hide substance in solution in the different liquors were:—*A*. 0.056 per cent.; *B*. 0.128 per cent.; *C*. 0.296 per cent. This explains the rapid increase in alkalinity with the sulphide and lime together, and also the rapid loosening of the hair.

Experiments were also made on the same lines as above, but with the sulphide and the lime mixed in different ways. In one case slaking the sulphide and lime together, in another case slaking the lime with a strong solution of the sulphide, and in another case slaking the lime with water, then adding the solution of sodium sulphide. The three mixtures, made in the above way, were then diluted with water to the required strength and pieces of hide immersed in the weak liquors. No differences could be

Digitized by Google

detected, in the decrease or increase of alkalinity, in the absorption of sulphur, or in the amount of hide substance dissolved.

DISCUSSION.

The chairman asked why caustic soda should not do the work better than a mixture of lime and sodium sulphide? The effect produced by the latter reagents might actually be due to the fact that there was a formation of caustic soda.

Dr. Gordon Parker said that the whole process of liming hides and skins preparatory to tanning had been much neglected by chemists in the past. More attention had been given to the constitution of the tannins and the tanning process in general, and the processes whereby the hides and skins were prepared for tanning had, with but few exceptions, been left severely alone. He thought now that chemists had begun to realize that one of the most important processes in connection with leather manufacture was the preparation of the raw pelt prior to the subsequent tanning. There were more chances of loss and more likelihood of trouble than in the tanyard proper. Years ago it used to be the general impression that the sole object of liming hides was to dissolve the hair-roots, swell the fibers, and kill the grease, so that the hair could be pushed off by mechanical means, and it was generally believed that the lime and the lime alone was responsible for this action. Payne and Pullman, in order to save the usual lengthy period of liming hides, patented a process by which lime was formed in the interior of the hide, by first placing it for a few hours in a solution of caustic soda, and afterwards in a bath of calcium chloride. By this means any proportion of lime could be rapidly and accurately introduced, and by this process the hides swelled rapidly. They were beautifully limed, but the hair remained as firmly fixed as ever, and it could only be removed by subsequently placing the hides into a solution of sulphide of sodium or into a pit containing a stale lime. To overcome this difficulty the hides were soaked prior to the patent liming process in an old stale soak to produce bacterial action. By this means hides could then be limed and unhaired in about 48 hours. It was now fully realized that bacteriological action played an important part in the unhairing of hides, and that the action of old

Digitized by Google

limes was largely bacterial and that hides could not be unhaired from a sterilized lime. He had been much interested in Mr. Blockley's experiments, which he thought had not been carried far enough as regarded the various compounds which were formed in the mixture of sodium sulphide in different proportions, and under different conditions. From the experiments it was impossible to detect any difference, but in practice one found, as far as one could gauge it technically, that there were differences. He believed that when the sulphide was mixed with the lime during slaking a better result was obtained, for he had generally found that the compounds, whatever they were, would unhair hides quicker than if sodium sulphide was mixed in the same proportion with the lime after it was slaked. A good way was to slake the lime with a solution of sodium sulphide in water. There were other methods whereby sulphide crystals were mixed with the lime and they were slaked together, but either of those methods in his opinion seemed to give better results than when the two materials were mixed cold and separate. The heat appeared to assist in forming some compound which had a greater or quicker depilating effect on the hides. One point referred to, the titration of the lime liquors, was very important. It was a very important matter nowadays when one understood how much hide substance could be lost by careless liming, to be able to titrate the lime liquor quickly, so that one could tell the foreman at once when to order the liquor to be run away. The zinc sulphate method hitherto used had not been found very satisfactory, and Mr. Blockey's modification would be of great assistance in the tannery. It would be also of great value if they could find out which of the possible materials was the active unhairing agent. If they knew that no doubt they would be better able to control the process.

Dr. H. G. Colman asked if there was definite evidence that the polysulphides were not more active substances than the sulphides in the process, and whether any experiments had been made as to the effect of increasing the amount of polysulphides in the mixtures used.

Dr. S. Rideal asked if spent gas lime ("Blue Billy") had ever been used as a depilatory in tanning, to get over the difficulty of

Digitized by Google

any free caustic soda, which might have an adverse effect. In the gas industry small quantities of sulphuretted hydrogen were determined colorimetrically with a sugar solution of lead acetate, which kept the lead sulphide in solution instead of precipitating it. If sugar was added to the tanning liquor a similar reaction might be used in determining the sulphide.

Mr. Blockey, in reply, said he thought it could be stated pretty definitely that caustic soda was not the active principle in the removal of the hair. It probably showed its effect in the extra swelling of the pelt; there was no loosening of the epidermis or the hair cells.

The Chairman asked with regard to the amount of hide substance that passed into the solution, whether the same effect was produced if it were placed in caustic soda. Had that been measured?

Mr. Blockey said that some was dissolved, but nothing like the amount which went into solution when a mixture of sodium sulphide and lime was used. He believed that in practice differences were obtained between the pastes made in different ways. These experiments were not meant to be taken as conclusive against that idea; they were done to determine, if possible, which were the active substances. They hoped to determine what the actual differences were between these compositions made in different ways. So far they had obtained no differences whatever in the chemical analyses. He did not think calcium polysulphide was at all likely to be formed, using the proportions commonly used in practice; qualitative reactions for polysulphides furnished no evidence whatever. He did not know whether any experiments had ever been tried on the actual unhairing action of calcium polysulphides, but he saw no reason why they should not have the power of loosening hair. The compound formed when sulphuretted hydrogen was passed into lime was known to leather chemists, and he understood from Dr. Parker that it had been used as a depilatory in bygone days.

Digitized by Google

ANALYSIS OF SULPHITE-CELLULOSE EXTRACTS.

By Frank M. Loveland.

It has been the lot of the writer, during the past few months, to hear a great deal of argument pro and con in regard to so-called Sulphite-Cellulose Extracts. At the time this is written nothing definite has been done in regard to the proper method for making an analysis of same. Many chemists have expressed their views as to the merits of these extracts, and what they intend doing with them. The whole situation has led to much talk and more bitter feeling than perhaps we can see from the outside.

Committees have been formed and undoubtedly work has been outlined. The writer has done no work on these extracts through committee, and what has been done in person is beside the mark. What seem important to be brought out are the real facts in the case as they confront us, not a new method of analysis. Perhaps what is here offered may be considered out of place in this JOURNAL: nevertheless, it would seem that it is time to bring the matter to notice. There has been too much talking in private and not enough in the open.

It also might be added that the writer is no advocate of sulphite-cellulose extracts, being interested in them solely from a tannery point of view. It is in the tannery that they must prove their worth or otherwise, and the whole interest centers around this pivot. There are men on the road selling this product who seem well able to take care of that end of the business. Having nothing in common with them, any criticism for what is written should not fall on their shoulders.

The facts of the case are that we are spending too much time in quibbling and splitting hairs about the analysis of this sort of extract and not enough time in the analysis of the situation. If we would come down to earth for a few minutes, get outside the laboratory, and call a spade a spade, we would come nearer to some logical conclusion. In the first place, let us take a definite proposition, not sulphite-cellulose extracts in general, but Spruce or Muskegon extract for instance. Here are terms that all tanners understand, and when we bring the situation down to

Digitized by Google

the last process of analysis, we all have the tanner to look to for our livelihood.

The question is will Spruce or Muskegon make leather? Now if we put this question fair and square to all men interested we will get answers both in the negative and affirmative, and we will have to admit that the affirmative answers will not come exclusively from men who have it to sell. We have the word of an extract maker that any firms making a straight brand of extract have nothing to fear from Muskegon or Spruce. Surely if this be the case, it makes no difference to the makers of other brands how we analyze these extracts.

It does not appear that we as chemists have such a great barrier to surmount or a great difficulty to overcome. We have given an extract to analyze, let us call it Muskegon or Spruce. This is the name it goes by, this is the name it is sold under. Head your report with this name. Analyze according to the official method and state this under your report. If it is a blend of these with other extracts, you have your tests, say that it is a blend. The firms who make Muskegon or Spruce will have no objection, they sell under a trade name, and the men who object to these extracts will also be satisfied.

Our present method of analysis is like a trial by jury. The jury gives us a verdict, it may be right, it may be wrong, but it is the very best method of trial known to man, so we use it and abide by results. Up to this time our method of analysis of Spruce or Muskegon is the best we have according to our knowledge; let us abide by results until something better is given. We as chemists can show neither favor or prejudice, we are a fair minded jury.

But let us revert to the tanner, the man we have to consider, the man who buys the extract and pays the bills. The salesman comes along and has Muskegon or Spruce to sell; the tanner if he is a wise man, gives them a trial. This may bring a smile to some faces, but we do not have to go back very far to remember when chestnut and quebracho were first given trials. In some cases both were thrown bodily out of the tannery together with the salesmen, who had them to offer, yet some pretty fair leather is being put on the market to-day from these tannages.

Digitized by Google

So we will admit the tanner gives the extract a trial and we will also admit for the sake of argument that it works well in the tannery. The tanner is satisfied with price and product. He buys more and sends his chemist a sample for analysis. What are you as chemists going to do about it? The logical answer is analyze it of course, by the best method you have, and report it for what it is, Muskegon or Spruce. Surely you do not intend to lay the sample on the shelf and let the tanner wait for you to split hairs, quarrel and quibble over a method of analysis.

We also might say in passing that if we as the A. L. C. A. throw this extract out of our method, or as individuals refuse to analyze it, as some have said they would do, it would not of necessity close the doors of the extract plants. The tanner if he likes may go back to his old friend the Fairbanks with its hundred pound weights, and let our little Henry Trömner keep its own company.

Now let us take the other side of the situation, the tanner buys in this case also, but the product fails to give the desired results. The same thing does not always work the same way in different tanneries. The tanner will from now on fight shy of the product or any blend of it. He is like a once hooked fish, suspicious of the angler's lure. You head your report Muskegon or Spruce blends, or make a note of same and the tanner will drop this extract like a hot coal.

You will find that it makes no difference to the tanner if the matter absorbed by hide powder is termed tannin or tare on your report. He would not buy this extract if you sent him fifty reports gratis, lithographed or hand emblazoned, with a fac-simile of your signature in raised letters. He is through. He will neither swallow or take the stuff into his system by any other manner of assimilation, as some would have us believe.

The writer does not want to depreciate any man's work, who may be trying to find a better method of analysis for this product. If anyone knows a better method, let us have it. What should be brought out is this, we have the product, we must analyze it, and if we call it by its proper name we are working no injury to the tanner or The A. L. C. A.

Digitized by Google

WHAT IS TANNIN?

By Roy H. Wisdom.

Tannin, or tannic acid, according to the Century Dictionary is "a white uncrystallizable inodorous substance, $C_{14}H_{10}O_9$, having a most astringent taste, without bitterness. It is very soluble in water, much less so in alcohol. It has an acid reaction and combines with most salifiable bases. It precipitates starch, albumin, and glutin, and forms with gelatine a very insoluble compound which is the basis of leather, and on which the art of tanning is founded. *The word tannin has been loosely applied to all astringent vegetable principles.*"

Professor Procter in his "Principles of Leather Manufacture" defines tannin as follows:—"The tannins, though varying considerably in their chemical constitution and in many important characteristics, are all marked by the power of precipitating gelatine and some allied bodies from their solutions, of converting animal skin into the imputrescible material known as leather, and of forming dark-colored compounds with ferric salts which are often utilized as inks."

In the analysis of a tannin bearing material, the chemist reports as tannin the result obtained by the present hide powder method. This is generally understood to mean tannic acid. On the interpretation of this word *tannin* in the analysis rests considerable responsibility, for the product we call leather must be judged accordingly. Should we revert to the old Lowenthal permanganate method which determines what is chemically known as tannic acid, and analyze some of the tanning materials now on the market, we would be confronted with results widely divergent from those obtained by the hide powder method.

It is just here that the question of tannin comes in. It seems to the writer that there is a considerable question as to whether the words *tannin* and *tannic acid* are synonymous for while both results are probably correct as to what they estimate, the tannic acid shown by the Lowenthal method is by no means the same as the tannin reported by the hide powder method. In other words, while each fulfills the definition of tannin, is it not true that the matter going to form the tannin of the hide powder

Digitized by Google

method is essentially something beside the tannic acid reported by the Lowenthal method?

Again returning to the Century Dictionary we find:—"The word tannin has been loosely applied to all astringent vegetable principles." Is this not an admission that perhaps after all, tannin is something more than tannic acid?

This also brings up the question—what is vegetable tanned leather? Again we call upon the Century Dictionary and find the following:—"The peculiar character of leather is due to the chemical combination of tannin in the process of tanning, or of tannin and *vegetable extractive matter* with gelatin as contained in animal skin; its physical characteristics, such as flexibility, tensile strength, color, and durability, are more or less modified by the processes subsequent to the chemical, and included in the various operations of currying and dressing."

Professor Procter says, "The object of tanning has been stated to be the rendering of animal skin imputrescible and pliable."

A few years ago at a meeting of the American Leather Chemists Association, considerable differences of opinion were expressed as to whether a certain sample submitted was really leather or not. The sample in question was a piece of animal skin which had been rendered "imputrescible and pliable" by treating with an extract which showed most marked differences when analyzed by the two methods above referred to. Inasmuch as this product fully conforms to the definition of leather as laid down in the Century Dictionary, being "due to the chemical combination of tannin in the process of tanning or of tannin and *vegetable extractive matter* with gelatin as contained in animal skin" and is to all physical intents and purposes, leather, is it not fair to assume that the amount reported as tannin by the hide powder method expresses as nearly as possible in figures, the leather forming properties of the material under consideration?

In conclusion then, does not the question resolve itself into a separation of the terms *tannin* and *tannic acid;* the former including tannic acid and vegetable extractive matter which combines with the gelatine in the skin, rendering it imputrescible and pliable, and the latter, meaning simply the chemical substance known as $C_{14}H_{10}O_9$.

Digitized by Google

EXTRACTS OF CELLULOSE.[1]

By M. Louis Sody,
Professor in the Tanning School at Liége.

Origin of these extracts.—The great and ever increasing use of paper long ago rendered it necessary to find sources of raw material in addition to the rags, of all sorts, old rope, tow and old paper which had long sufficed for the manufacture of paper. Analysis having shown that the cellulose of plants is essentially similar to the material of rag papers, attention was naturally directed to the vegetable kingdom in the search for a substitute for rags.

The problem to be solved in the chemical production of wood pulp consisted in extracting from the woody tissues the cellulose which they contain, in such a condition of length, strength and elasticity that it could be felted together in the manner essential to the making of paper. There are evidently many possible ways of extracting the cellulose from wood, but a study of them is foreign to the purpose of this lecture. The system most used in the making of wood-pulp is as follows: The wood is reduced to small chips by a suitable machine, or ground in a mill, so as to expose as large a surface as practicable to the action of the chemicals. The chipped wood is placed in autoclaves or specially constructed vats, where it is treated with a solution of acid calcium sulphite ("bisulphite of lime"). The wood is thus disintegrated, the cellulose remaining undissolved in a more or less pure form, having a yellowish color. The liquid which flows away is brownish black. This liquid holds in solution the tanning matters, carbohydrates and salts.

Since no way of utilizing this liquid had been discovered, it was formerly turned into the streams, producing great pollution of the water. The nuisance to those who lived along the streams became unbearable, and a law was passed forbidding the diversion of these wastes into the streams. Being thus compelled to find means of disposing of these residues, the manufacturers sought for a market for the matter contained in them. Chemists at-

[1] Lecture delivered May 10, 1912, before the "Chambre syndical de la Tannerie," of Brussels. Translated from *LaHalle aux Cuirs*. Also appeared in the Bulletin of the Bourse aux Cuirs at Liege.

Digitized by Google

tacked the problem, and considering the composition of the wood before being treated with bisulphite, they reasoned that the residue ought to contain tannin. We know that wood is made up of cells whose walls are of cellulose, vasculose and cutose cementing these cells into the vessels and fibers, which make up the organic tissues. Finally, the cavities of these cells are filled with amidon, gums, resins, and tannin, which together with mineral salts make up the chemical constitution of the plant. Since the manufacturing process separates the cellulose from all the other materials, a considerable amount of tannin ought to be found in these residues. They cannot be used directly to make leather, not only on account of their dilution, but also because of the presence of too great proportions of lime and of bisulphite. Such a tanning material would make brittle leather. The presence of these substances is not, however, an insurmountable obstacle to the use of these wastes in the tannery; special processes have been devised to neutralize the injurious effect of these various substances. After this treatment the liquor is concentrated, and a new tanning material takes its place among the many products offered to the tanner.

This new substance, so-called tanning material, was introduced successively into England, Germany and Austria. It appeared in Belgian markets two or three years ago, but has not as yet come into extensive use.

Is the pulp extract a tannin?—What is the chemical constitution of this product, and can we consider it a tannin? The chemical nature of tannin is not well understood, so that in order that a substance may be considered a tannin we say that it must respond to certain tests. It must, first, have an astringent taste and a feebly acid reaction; second, it must precipitate the alkaloids and gelatine from their solutions; third, it must precipitate certain metallic salts, such as ferric chloride, and with this it must make a black, green or blue coloration; fourth, it must combine with alkalies to from products which blacken when oxidized by exposure to the air; fifth, it must unite with skin tissues to form an imputrescible substance called leather; sixth, it must dissolve in water, alcohol and acetone and be insoluble in chloroform, carbon disulphide and ether.

Digitized by Google

Cellulose extracts do not fulfill all of these conditions. That is why they are not considered to be tannin in the same sense as quebracho, chestnut, oak and mimosa. This substance is not a tannin extract, but is, as we have seen from considering its mode of manufacture, a concentrated solution of vegetable matters from the substance of the wood, containing certain colloidal substances absorbable by hide powder, as are certain other non-tannins, such as gallic acid.

There are on the market different kinds of cellulose extracts of varying degrees of concentration, and differing in the proportion of tannin to nontans. The nontans include many substances both mineral and organic. The percentage of mineral matters may be as high as 9 per cent., including salts of lime, of magnesia, of manganese, and even of iron and alumina. The organic nontans are largely carbohydrates, and of these the most part are reducing sugars, since the amount of Fehling's solution reduced is not increased by acidification.

Analysis of these extracts by Procter's filter-bell method indicates a tannin content from 20 to 30 per cent., and nontans from 20 to 37 per cent. But the filter-bell method is not a scientific method; it shows the matters absorbable by hide powder, while the scientific method of Löwenthal is based on the oxidation of the tannin by permanganate. This method gives a tannin figure for cellulose extracts about one-sixth as great as the filter-bell method. This difference in results is explained by the fact that the potassium permanganate indicates with considerable accuracy the quantity of gallo-tannic acid present. The quantity of gallo-tannic acid in the cellulose extract is therefore only that shown by its reducing effect on the permanganate.

M. Lepetit has found a term well adapted to this sort of extracts. He calls them pseudo-tannins. The cheapness of these extracts is an invitation to fraud and they are found mixed with other extracts in the market, mainly chestnut. The hide powder method does not show its presence, but the permanganate method has cooled the enthusiasm of the adulterators. This method not only shows the presence of cellulose extract, but even permits the amount added to be estimated.

Procter has worked out a method for detecting the presence of

Digitized by Google

sulphite-cellulose in extracts. Since aniline is the test for ligneous materials, the presence of this substance may be detected in the following manner:—To 5 cc. of a tannin solution, add one-half cc. of aniline; shake; add to the mixture 2 cc. concentrated hydrochloric acid. This addition of acid immediately clears up the slight cloudiness caused by the aniline, giving a clear solution whenever cellulose extract is absent. If such extract be present, an abundant precipitate forms, which gradually rises to the surface. If this test causes a slight cloudiness only, the presence of cellulose extract is not proved since such a result may be due to faults of manufacture in an extract which has not been sophisticated.

Other methods of detecting cellulose extract might be mentioned, but of all the means tried at the Liége Tanning School, none has given results so satisfactory as the titration with potassium permanganate and the phenylamine test. We have mixed quebracho extract with cellulose extract and percentages of tannin as shown in the following table were obtained, using the hide-powder (shake) method and the method of Löwenthal.

Quebracho per cent.	Cellulose per cent.	Tannin	
		Hide-powder	Löwenthal
Pure	—	36.0	35.3
20	80	32.8	10.2
40	60	33.5	16.4
60	40	34.1	23.4
80	20	35.3	29.3

Finally, Yocum and Faust, in an article published in the Journal of the American Leather Chemists Association, (VI, 537), make an interesting observation: When sulphite cellulose extract is mixed with a tanning extract, loss of tannin takes place, and this loss is greater where the proportion of sulphite-cellulose extract is greater. Exceptions are noted in the case of sulphited liquid quebracho, and in one or two other instances where the proportion of sulphite-cellulose was only 10 per cent. A mixture of equal parts of cellulose extract and chestnut showed a loss of 6 per cent., a similar mixture with myrobalans from 3 to 4 per cent. and valonia nearly as much. Another American chemist, Mr. H. C. Reed, has offered an explanation of these facts: Hide powder placed in contact with a mixture of cellulose and

Digitized by Google

chestnut extracts, absorbs first the tannin of the chestnut, and being then partially tanned has less power to absorb the cellulose extract than untanned hide powder. This explanation assumes that hide has not so great an absorptive power for cellulose extract as for the other tannins. In a mixture of cellulose extract and sulphited quebracho, such action was observed, but in a much smaller porportion. Some mixtures were analyzed with the following results:

Tannin found per cent.	Theoretical tannin per cent.	Non-tan found per cent.	Theoretical non-tan per cent.
10.3	11.47	6.3	5.18
8.24	8.92	8.3	7.56
5.82	6.35	10.64	9.94

We have performed about a score of analyses of mixtures, and in every case have found less than the theoretical amount of tannin, and therefore higher nontans.

Use in the tannery.—I have reviewed the history of cellulose extracts, and indicated their special characteristics: the most important question remains to be discussed. What is the value of cellulose extracts in the tannery, and can they be employed with success? Aided by Messrs. C. Hendricks and René Lefebvre, I have made some experiments in tannage at the Liége Tanning School. I wish to thank my two collaborators and to say that if my work yields results of value, a good share of the credit is theirs.

A strip of hide as uniform as possible in thickness and condition was cut into pieces of similar size and as nearly as possible of the same weight. The different samples varied in thickness from 3.3 to 3.5 mm. After being well washed they were placed in a 0.25 per cent. solution of boric acid for 24 hours. Boric acid was chosen as the plumping agent because of its moderate action.[1] The thickness of the samples after treatment with boric acid varied from 3.5 to 3.8 mm., and their weights from 40 to 45 grams. We then tanned the pieces in liquors made up and analyzed in advance, as follows:

[1] Wood, Hough and others say that boric acid has no plumping effect.—EDITOR.

Digitized by Google

No.	Composition	Density Baumé	Total extract per ct.	Tannin per cent.	Non-tans per ct.
1	100% quebracho	8.8 at 16° C.	16.30	14.57	1.73
2	75% quebracho, 25% cellulose	9.5 at 16° C.	16.46	10.30	5.5
3	50% quebracho, 50% cellulose	9.4 at 16° C.	16.54	8.24	8.3
4	25% quebracho, 75% cellulose	8.8 at 16° C.	15.80	5.82	10.64
5	100% cellulose	9.5 at 16° C.	16.00	3.68	12.32

A rapid method of analysis was used, that is to say instead of chroming the hide powder, washing it, etc., we mixed a known weight of hide powder with the tanning solutions to be tested. Corrections were necessary on account of soluble matter in the hide, etc.

The samples of hide with their liquors were placed in bottles and stood for some hours. The rotary shaker was then started, and after 29 hours of rotation the samples were examined. They seemed to be completely tanned. They were, however, shaken 10 hours longer, then washed, and after soaking in pure water for 15 minutes, weighed. The rendement, for 100 parts white weight was as follows:—The leather tanned in liquor No. 1, 119.5 per cent.; No. 2, 109.5 per cent.; No. 3, 106.5 per cent.; No. 4, 117.5 per cent.; No. 5, 116.5 per cent.

The appearance of the samples varied considerably. That tanned in pure quebracho was red, and firm to the touch; that from liquor No. 2 was brownish and fairly firm; that from No. 3, dirty gray, supple and soft; that from No. 4, grayish and very soft; that tanned in pure cellulose extract very soft and light yellow. In order to estimate the tannage, cuts were made in the samples, and they were found to be completely tanned. The pieces were smoothed, lightly oiled on the grain to prevent oxidation, and suitably dried. The spent liquors were analyzed, with the following results:

No.	Density Baumé	Total extract per cent.	Tannin per cent.	Non-tans per cent.
1	7.0 at 21° C.	12.29	11.13	1.16
2	6.9	12.11	7.22	4.88
3	7.4	13.06	5.62	7.44
4	8.0	13.07	3.94	9.76
5	8.3 at 19° C.	14.12	2.48	11.64

Comparing the new and spent liquors we find a tannin absorption varying according to the proportions of cellulose extract

Digitized by Google

employed. The tannin absorbed from liquor No. 1 was 3.44 per cent.; from No. 2, 3.08 per cent.; from No. 3, 2.68 per cent.; from No. 4, 1.88 per cent. and from No. 5, 1.20 per cent. After drying, the pieces were again examined, and here a surprise greeted us. While all the pieces had before drying semed perfectly tanned, it was now seen that only the sample tanned with pure quebracho was really tanned. The others showed a distinct line in the middle, which was more pronounced in proportion as the proportion of cellulose extract was higher.

The rendements of finished leather based on 100 parts white weight were: No. 1, 66.3 per cent.; No. 2, 61.7 per cent.; No. 3, 59.4 per cent.; No. 4, 57.5 per cent.; No. 5, 53.8 per cent. These results scarcely need explanation. A glance at the table sufficiently indicates the action of cellulose extract on tannage. This result is scarcely surprising, after the studies undertaken by various chemists, especially the work of Parker and Blockley recently published in *Collegium* on the value of nontans in tannage. It had been previously supposed that nontans easily penetrated the fibers of the leather and gave a higher rendement. It had also been said that particularly in drum tannage a high percentage of nontans had a good influence. These gentlemen have shown that up to a certain point the nontans in an extract may penetrate the fibers and give weight to the leather. They conclude from their experiments that a high proportion of nontans does not tend to make either firmer or heavier leather. This study was very interesting, and bears upon the subject we are discussing, for we found that in proportion as the nontans were increased by addition of cellulose extract, the rendement decreased. I believe that cellulose extract employed in mixtures with other extracts is an obstacle to tannage in a drum. In vat-tannage this extract may give rise to the acids necessary to the plumping of the hides, but may through the weakening of the liquors, diminish the rendement.

We wished to verify the rendements by analyzing the pieces of leather, thus learning the proportions of hide and of combined matter in each. The nitrogen was determined by the Kjeldahl method. This method enables us to follow tannage through its various phases. The proportion of hide diminishes

Digitized by Google

as tanning proceeds, and the combined tannin increases until the hide has taken up all the tannin with which it can combine.

The following results are from the dried and extracted leather: Percentage of hide-substance in No. 1, 58.57; No. 2, 64.13; No. 3, 67.17; No. 4, 67.30; No. 5, 74.35. On an air-dry basis, these give the following figures:

Number	Hide substance per cent.	Combined tannin per cent.
1	43.30	30.58
2	46.25	28.29
3	49.57	24.23
4	49.02	23.82
5	51.39	17.73

One may ask after this study, of what value cellulose extract is. We have placed a piece of quebracho tanned leather in a solution of cellulose extract of 9°Bé, for some hours, with agitation. The leather so obtained was treated in the same manner as the other pieces, dried and weighed. The rendement was raised from 66.3 per cent. to 70.9 per cent. by the retannage. This leather was analyzed to find out whether a part of the tannin of the cellulose extract had been fixed upon the hide. But on washing in water the materials which had raised the rendement were nearly all washed out. Cellulose extract may be used for retannage of leather in place of such other extracts as cutch and gambier, and may advantageously replace glucose and molasses. Beside this value as a retanning agent, cellulose extract has another advantage which is peculiar to itself; it acts as a decolorizer. Quebracho, mangrove and divi-divi leathers have a very disagreeable brown color. Cellulose extract corrects this color most satisfactorily. A solution having 75 per cent. quebracho and 25 per cent. cellulose gave a leather of a light rose-color; equal parts gave light brown and 25 per cent. quebracho and 75 per cent. cellulose gave light yellow. Pure cellulose extract gave a yellow leather which shrivelled in drying. Leather tanned with quebracho having a disagreeable red color is changed to a color similar to that of oak leather by retannage with cellulose extract.

An equally interesting point is in regard to the drying of leathers tanned with mixtures of cellulose extracts, especially

Digitized by Google

retanned leathers. It is well known that light has an influence on the color of some tannages. Youl and Griffith made experiments to determine the actual effect. They found that the tannages least affected were those of oak-wood extract, chestnut extract and valonia, while leathers tanned with quebracho, mimosa and hemlock were much darkened. We found that when a part of one of our pieces tanned with mixtures of cellulose extracts was exposed to the light while drying, the part exposed was much darker in color. It is therefore important not to expose retanned leather to the light while drying.

BOOK NOTICE.

THE PUERING, BATING AND DRENCHING OF SKINS. JOSEPH T. WOOD. Spon and Chamberlain, New York, 1912. 300 pages, 8½ by 5½ inches. 33 illustrations. Bound in cloth. Price $5.

The chapter headings in this book are as follows: I, Description of the Puering and Bating Process. II, The Chemistry of Bating. III, The Physics of Bating. IV, The Bacteriology of the Bate. V, Action of Enzymes. VI, Original Papers on Bating. VII, Artificial Bates. VIII, Patents. IX, Drenching. X, Original Papers on Drenching. XI, Bibliography.

The papers included in chapter VI are: (1) Fermentation in the Leather Industry, (part relating to puering and bating); J. Soc. Chem. Ind. 1894, p. 219. (2) Notes on the Constitution and Mode of Action of the Dung Bate in Leather Manufacture.. J. S. C. I., 1898. p. 1010. (3) Further Notes on the Action of the Dung Bate. J. S. C. I., 1899, p. 990. The papers in chapter X are: (1) Further Contribution on the Nature of Bran Fermentation. J. S. C. I., 1893, p. 442. (2) On a Pure Cultivation of a Bacillus Fermenting Bran Infusions. J. S. C. I., 1897, p. 510.

The author is a director in the firm of Turney Brothers, manufacturers of light leather at Nottingham. His long connection with this business has given him opportunities for the practical

Digitized by Google

study of the action of bates, and he has made many scientific investigations in the same field which have brought his name into prominence wherever the scientific study of the processes of leather manufacture is being pursued. In the preface Mr. Wood expresses regret that his increasing absorption in the commercial side of the business has compelled him to discontinue his studies in the bacteriological and other features of the bating, puering and drenching processes. This regret is shared by every leather chemist in the world, and most by those who have made a feeble beginning in the study of the same difficult and complicated problems in which the author has made such signal progress. To his unexcelled knowledge of his subject, Mr. Wood adds the happy faculty of telling that he knows in a style of great simplicity and clearness. Altogether, the book is a very valuable addition to the literature of leather manufacture.

ABSTRACTS.

The Acidity of Tan Yard Liquors. HUGH GARNER BENNETT. *S. and L. Rep.*, April 18, 1912. All tan liquors are acid, and the acid plays an important part in the process of tanning, first in neutralizing the lime in green goods and afterwards in plumping the same goods. Yet about all we know of the function of this acid other than the points just noted is that the "sourer" (*i. e.*, the more acid) the liquor, the more weight and firmness is obtained in the finished leather. No chemist has yet devised a satisfactory method of estimating the acid in a tan liquor, or even in agreeing with other chemists as to what he is trying to estimate. Yet every year are published new methods of determining the acidity of tan liquors, and every year they are tried, discussed and discarded. *The "charcoal method"* of Simand consists in boiling the tan liquor with animal charcoal to remove tannin and titrating the residual liquor with standard alkali. This method has been shown to be unsatisfactory. *The gelatin precipitation method,* suggested originally by Koch, has been widely used in various forms, modifications having been proposed by Paessler, by Procter, by Reed, and by Yocum. The method consists essentially in precipitating the tannin by means of a gelatin solution, and titrating the filtrate. By this method the correct result can only be obtained by a compensation of errors. The gelatin precipitate always absorbs acid, and

Digitized by Google

if the gelatin be in excess the error is considerable. If, on the other hand, the tannin be slightly in excess, the filtrate on titration with standard alkali gives a very indefinite end-point owing to oxidation. No modifications seem to overcome these difficulties. Alcohol (Reed) and salt (Procter) certainly make the precipitate more compact but do not prevent the absorption of acid. Gum arabic (Yocum) may precipitate some gallic acid, but not all, and is itself of variable acidity. Various indicators have been proposed to be used with this method, but the writer prefers phenolphthalein, though he thinks hematin might be employed. There seems to be no way of overcoming the absorption of acid by the precipitate, and this seems a fatal defect to its measuring the acidity accurately. The writer has found that if this method be carried out always under the same conditions of detannization, results may be obtained in which the errors involved may not only be reduced to a minimum, but be made approximately constant. Hence comparative results may be obtained, which yield very interesting and useful information to the tanner. The writer finds that this may best be accomplished by diluting the liquor always so as to contain 0.4 per cent. of tannin, and adding 25 cc. of a 0.2 per cent. gelatin solution to 25 cc. of the diluted liquor. An aliquot portion of the filtrate from this is titrated with decinormal caustic soda and phenolphthalein. *The hide powder method* gives bad results. *The quinine method* of Hoppenstedt, which depends in principle upon the detannization of the liquor by means of quinine, which is added in alcoholic solution, is unsatisfactory. The tannates of quinine are not all insoluble, and indeed are of varying solubility. *The magnesia method* of Kohnstein & Simand involves detannization by means of boiling the liquor with magnesia. Not all tannates of magnesia are insoluble, and gallic acid is not precipitated. *The basic dye method* of Reed depends upon the precipitation of tannic by means of a basic dye. There is no basic dye which will precipitate completely all the tannins. *The formaldehyde method* of Stiasny involves detannization by means of formaldehyde. It is professedly applicable only to liquors which contain catechol tans only. *The fluorescein method* of Jones has proved very disappointing to the writer. The liquor is titrated direct until excess of alkali shows fluorescence with the indicator. In the writer's experience fluorescence has always been observed before the titration has commenced, doubtless owing to the fact that acetic acid has been present in the liquors, which acid causes fluorescence with the fluorescein indicator. The method of titrating to a "maximum fluorescence," suggested by Jones, has proved quite inadequate to cope with this difficulty. The method, moreover, is wrong in principle, as fluorescein is an indicator sensitive to weak acids, and hence also to tannin. In any set of liquors the method, if workable, would only estimate roughly the tannin content, which is the predominant acidic content. *The carbon dioxide method* of Fiske depends upon the action of the tanning liquor on calcium carbonate, the liberated carbonic acid being collected in potash and weighed. Here also tannin is estimated, for

Digitized by Google

tannin will liberate carbonic acid from chalk, especially on heating. *The distillation method* suggested first by Procter and recently revived by Grasser, has proved in the writer's hands wholly unsatisfactory. The acids which it is chiefly desired to estimate, viz., acetic, lactic, formic, etc., are not volatilized easily. Even when the method is carried out under the best conditions it is impossible for any two observers to obtain anything like concordance. Steam distillation improves the case very little. The writer has found, moreover, that liquors which contain any quantity of lime salts (as green liquors always do), give wholly abnormal results, owing to the action of tannin at boiling point upon these salts, causing liberation of the acids of the salts and the formation of tannates of lime, which are precipitated. Any method along these lines, therefore, seems doomed to failure. The lime water method of Procter, in which 10 cc. of the liquor are titrated with saturated lime water to a permanent turbidity, has proved in the writer's hands of considerable service. It is at any rate workable, and will measure accurately the extent to which a liquor will form soluble salts with lime, which information is useful in the case of green liquors. As a method for estimating the acidity of liquors, it is, however, quite misleading, its chief defect being that the tannin is estimated. In all tanneries the amount of tannic acid is much greater than the amount of other acids, so that the lime water method as it stands simply measures somewhat inaccurately the tannin content, or more correctly, the total acidity of the liquor. The writer has to some extent overcome this difficulty by diluting the liquor to be tested so that it always contains 0.4 per cent. of tannin. In this case therefore, the error due to tannin is constant, and the results are comparable at any rate, both in different parts of the same tannery and at different times. Useful information may be obtained in this way, but as the operation involves a preliminary analysis for tannin, and as the results are only empirical even then, this mode of procedure will not be encouraging to many workers. Furthermore the writer has proved that the error due to tannin is only a constant for any one tannin, or blend of tannins. Each tannin even in 0.4 per cent. solution, will dissolve a different amount of lime. Hence practical results are only comparable when the same blend of materials is being used. Hence also the results from different tanneries cannot be compared. *The direct titration method* recently suggested by Procter and Jones is, like the fluorescein method, wrong in principle. If indicators like hematin, phenolphthalein, etc., be employed, which are sensitive to weak acids, then the direct titration method estimates merely the total acidity of the liquor, *i. e.*, that due to tannin plus gallic acid, plus acetic acid, etc. If, on the other hand, indicators like Congo Red, methyl orange, etc., be employed, which are insensitive to weak acids, then the results are determined wholly by the dilution of the tannins and are not at all influenced by the acids which it is chiefly desired to estimate, *e. g.*, acetic acid. *The electrometric method* of Wood, Sand & Law is a welcome method inasmuch as it estimates something definite,

Digitized by Google

viz., the hydrion concentration. For theoretic investigations this will doubtless prove of service, but for practical purposes it must be criticised on the ground that tannin is estimated by it. Moreover this fact seriously damages the claim of the authors that the results of this method are intimately connected with the "plumping power" of a liquor. The tannins contract the hide rather than plump it, and hence the results, which include the tannin of a liquor cannot be proportional at all to the plumping power of a liquor. *The lead oxide method* which was suggested a few years ago by the writer and Mr. C. W. Wilkinson involves detannization of the liquor by means of lead oxide. This reagent was chosen because the lead salts of all tannins are insoluble. It was chosen also because the lead salts of gallic, sulphuric, carbonic, boric and oxalic acids are also insoluble whereas the lead salts of acetic, lactic and formic acids are soluble. Thus tannin and its decomposition products may be completely excluded, and only the true plumping acids determined. Liquors are not easily detannized by the reagent, and owing to the great excess of tannin over the other acids it is desired to estimate, the results are often of doubtful value. This difficulty has been largely overcome by using liquors diluted to contain a constant amount of taninn. In 0.4 per cent. solution, lead oxide will precipitate practically all the tannins when digested with the liquor in the cold for about half an hour. By operating thus very interesting and important comparative results may be obtained. The acids present in the filtrate as lead salts of varying basicity, are best estimated by titration direct with caustic potash and phenolphthalein. The results obtained in this way are much lower than those obtained by other methods, but are in the writer's opinion still too high, and he hopes by varying the concentration and temperature of the liquor to differentiate accurately between the true plumping acids and the test of the acidic content of a tan liquor.

Swelling and Solubility of Hide by Acids. ALEX. T. HOUGH. *Leather World,* IV, 190-2, 268-9. The author describes experiments which aim to be practical in their character. Care was used to keep working conditions uniform, and carefully standardized solutions were used, so that the results are comparable, even if not accurate in the scientific sense. The hide powder used was American Standard, acidity 5 cc. N/10 alkali per 6.5 grams dry hide, moisture 13.5 per cent. To estimate the swelling power of the various acids, the equivalent of 2 grams dry hide powder was placed in a graduated cylinder and 50 cc. of the acid solution added with a pipette. The whole was well shaken, and shaken repeatedly during 2 hours. The mass was then turned out on a tared filter and allowed to drain for 1 hour, well covered to prevent evaporation. The filter and swollen hide were then weighed. The solution drained from the swollen hide powder was then titrated back to get the acid absorption, and where possible a portion was evaporated to find the solubility of hide substance in the particular solution used. In column 4 of the table, the weight of

Digitized by Google

1 Reagent 50 cc.	2 Residue 10 cc.	3 Acidity titrated back on 10 cc.	4 Weight of powder	5 Acid absorption per 2 grams hide-powder	6 Remarks
Water	8 m.g.	—	18.430	—	—
N/100 hydrochloric acid	5 m.g.	1.0	28.114	37.5 cc. N/100	10 cc. acid = 8.8 N/100
N/10 hydrochloric acid	17 m.g.	6.7	33 230	15.0 cc. N/10	—
N/1 hydrochloric acid	22 m.g.	9.3	17.140	20.0 cc. N/10	—
N/100 sulphuric acid	4 m.g.	1.0	21.005	38.5 cc. N/100	10 cc. acid = 9.0 N/100
N/10 sulphuric acid	—	7.0	27.823	13.0 cc. N/10	—
N/1 sulphuric acid	—	9.3	21 566	20.0 cc. N/10	—
N/100 formic acid	5 m.g.	3.1	24.314	29.5 cc. N/100	10 cc. acid = 9.3 N/100
N/10 formic acid	14 m.g.	7.4	38.882	11.5 cc. N/10	—
N/1 formic acid	19 m.g.	9.6	39.968	5.0 cc. N/10	—
N/100 acetic acid	7 m.g.	6.0	19.735	18.5 cc. N/100	—
N/10 acetic acid	13 m.g.	8.4	31.900	6.5 cc. N/10	—
N/1 acetic acid	21 m.g.	9.3	40.170	20.0 cc. N/10	—
N/100 lactic acid	—	2.4	24.500	36.5 cc. N/100	—
N/10 lactic acid	—	7.5	38.740	11.0 cc. N/10	—
N/1 lactic acid	—	9.6	38.285	5.0 cc. N/10	—
N/100 oxalic acid	—	1.1	21.910	43.0 cc. N/100	—
N/10 oxalic acid	—	4.3	38.412	27.0 cc. N/10	—
N/1 oxalic acid	—	9 2	27.775	25.0 cc. N/10	—
N/100 boric acid	2 m g.	9.7	8.898	Nil.	—
N/10 boric acid	—	9.7	10.124	Nil.	—
Sat. boric acid	—	7.6	17.060	10.5 cc. N/10	10 cc. sat. BO_3H_3 = 8.05 N/1

Digitized by Google

the wet filter is included; this was nearly constant, about 0.9 gram. An important question in regard to the action of acids on pelt and leather is the relation of swelling and absorptive power to destructive action. Results obtained seem to throw some light on this question. The use of mineral acids and oxalic acid has been condemned by the book-binding committee of the Society of Arts because these acids cause gradual disintegration of the leather, as has been shown by the researches of M. C. Lamb. It will be noticed in column 4 of the table that the swelling power of the mineral acids and oxalic acid increases up to N/10, and is less for N/1 than for N/10.' All the other acids tested except lactic show an increase of swelling power up to N/1, and it remains constant, within the limit of experimental error. It is notable that boric acid produced less swelling than pure water. Another noticeable fact is that the swelling power of the acids seems not to bear any direct relation to the dissociation constant or to the hydrion concentration. This is probably due to the action of the other dissociated radicals present, which modifies the behavior of the hydrions. The comparative "strength" or degree of dissociation of the different acids is indicated by the following figures (see Procter, Tanner's Year Book, 1911; this J., VI, 442): hydrochloric, 200; sulphuric, 200; oxalic, 0.1; formic, 0.0214; lactic, 0.0138; acetic, 0.0018; boric, 0.0co,coo,01. It is evident that these figures are not at all proportional to the weights of the swollen hide. The other radical, or anion, must be the modifying factor. It is this radical which causes the enormous physical and chemical differences which exist between the solutions of different acids. Although the electrical charges of all the ions, positive and negative, are equivalent each to each, their affinities one for another are different, thus causing widely different dissociation factors, and upon these factors depend to a large extent the differing electrical conducting powers of the solutions. The varying rates of travel of the different ions also produce important effects. The swelling of hide powder in acids is thus a very complicated question, depending on all these electrical properties of solutions and ions. Other effects also come into play, such as osmotic or solution pressure.

Acids which swell pelt strongly will ultimately destroy its fibrous structure by removing the calcium base which is necessary to its existence. When the lime is removed the pelt becomes very soft, and is finally reduced to a solution. This happens when organic or mineral acids are used in too strong solution. Boric acid may be used without risk because of its weakness and limited solubility. All the acids tested except boric have a destructive action when used in too strong solution. In practice, at least in the case of sole leather, boric acid has no depleting effect, nor does it produce any swelling. In calculating the absorption it is necessary to take into account the dilution due to the added hide powder. The total volume added was estimated at 1.5 cc. per 50 cc. of acid employed, so that a correction of 0.3 cc. was added to the figures in column 3 in calculating column 5.

Digitized by Google

A portion of the hide is soluble in any solution unless it contains tannin or allied bodies, so that a certain amount of loss of hide substance is inevitable in the processes which precede tannage. These soluble bodies are less complex in their molecular structure than hide fiber, and are not fibrous in structure. They are known as proteids. Some are soluble in alkaline solution while some are precipitated by alkalies. Another group are soluble in acids. Those which are soluble in alkalies are generally precipitated by acids and vice versa. The skin fibers are not attacked by fresh lime solutions, but the interfibrillar substance may be entirely removed. In order, therefore, to make a full, firm leather, the hides should have a short, sharp liming, being then placed in acid deliming pits, in which the lime soluble compounds will be precipitated and thus saved to combine with tannin later and so help to fill the leather. The hide substance is also soluble in acids, although less so than in alkalies. The deliming process should therefore be also short. As soon as the hides are in a tan liquor, the liability of loss is much less. Very old liquors contain gallic acid and other products of fermentation which have a solvent action on hide substance. Liquors containing very little tannin may thus cause a considerable loss. Such liquors show by the Kjeldahl process considerable quantities of nitrogen. The early liquors should therefore be fairly strong, but not strong enough to cause drawn grain. Boric acid used in deliming tends to prevent drawn grain. The lower limit for the first liquor should be about 0.2 per cent. tannin.

In column 2 of the table, no figures are given in the cases where non-volatile acids were used, as it was of course impossible to dry the residue in those cases. In the case of N/100 boric and sulphuric acids, the residue of acid was regarded as negligible. The weighed residues in column 3 do not accurately represent hide substance, as they include soluble calcium salts. In the case of the stronger acids, the larger quantity of residue was probably due to these rather than to greater quantity of hide substance. The residue from water is greater than in the case of any weak acid of deliming strength, suggesting that the acids precipitate certain proteid bodies which are soluble in water.

The author assumes from the small residue in the case of N/100 boric acid that it dissolves no hide substance, and since none or very little of it is absorbed or retained by the hide he assumes that all its energy is directed to the removal of lime, and that it is therefore the most economical. Formic acid is superior to acetic in the matter of solution of hide substance, but is absorbed to a greater extent. It may be advisable to use formic if the early liquors are lacking in acidity, on account of its swelling properties. If boric acid has been used, the early liquors must be acid.

Meeting of the British Section, I. A. L. T. C., at Leeds, May 18. *Leather World*, May 23. M. C. Lamb was elected Treasurer. A resolution was adopted, recommending to the Executive Committee the week of Sept. 16

Digitized by Google

for the 11th conference of the International Association. Professor Procter, presiding, expressed the opinion that it would be better in future to fix upon some neutral place for the conferences, so that there would not be social diversions to interfere with the work of the conference. Several speeches were made felicitating Professor Procter on his election to the Freedom of the Leathersellers' Company. J. T. Wood gave a resume of his paper on the control of limes. Professor Stiasny discussed Kohnstein's method of estimating sulphuric acid in leather, and stated that in the presence of chlorides it was absolutely unreliable. It was decided to recommend to the Conference that all leathers be extracted at a temperature not to exceed 45° C. Dr. Parker gave some details in regard to the softening of dried hides with the aid of formic acid, claiming numerous advantages for this method. *Collegium* was adopted as the official organ of the British Section.

Professor Procter then called the attention of members to the fact that there was still a certain number of firms who desired analyses to be carried out by the old filter bell method; he pointed out that this was difficult to do, as the old hide powder did not exist, and that, dependant upon what powder was used, analyses by the old filter bell method could not be accurately reported to within 5 per cent. He also pointed out that even when using Professor Paessler's hide powder, the results were unreliable, as if one packed the filter bell tight one could get high results, and if the filter bell were packed loosely about 2 per cent. less tannin would be returned, even although the filtrate in each case was tested and found to be tannin free. He was of the opinion that every member of the I. A. L. T. C. should deprecate by every possible means the use of the old filter bell method of analysis, which had been proved to be inaccurate and highly misleading. This raised a discussion in which many members took part, and it was agreed that, while the members of the British Section could not refuse to carry out analyses by the filter bell method, if specially requested to do so, yet any analyst reporting an analysis by this method should, as the rules prescribe, state on his analysis form the exact details of the method used, and also point out that the method was inaccurate, and that the results as reported were unreliable. It was agreed that the British Section should take a firm stand on this question at the coming Conference in September.

Purging with Acetic Acid. ANON. *Leather Manufacturer*, XXIII, 207. Acetic acid is recommended for deliming skins for light leathers, because of its cheapness, because it can now be obtained in a high state of purity, because it forms a very soluble lime salt, and because it is harmless, and the excess is easily removed. The writer claims that this acid not only serves to delime the skin, but that skins so treated do not require puering.

Butyric Acid. *Leather Manufacturer*, XXIII, 209. (From an article in *Marche aux Cuirs* by Messrs. Caspari and Defais.) The unhaired and fleshed skins are washed, and then placed in a liquor of 1° bk. where they

Digitized by Google

are left 24 hours. They are then transferred to a liquor of 2° bk. to which has been added 4 oz. butyric acid for each 100 lbs. raw skin. Each day the strength of the liquor is increased, the quantity of acid being the same in all. This process, the writers claim, gives a good yield of leather whose grain is especially fine.

Belgian Hide Trade Methods. *Consular and Trade Reports,* June 15, 1912. The great majority of the hides brought into Antwerp are wet salted River Plate hides. On being unloaded, they are brushed to free them from salt, bundled, weighed and sorted. There are three classes and various sub-classes. This sorting is done under the supervision of representatives of a single firm who act as official hide brokers, and through whom nearly all the dealings in hides in the city of Antwerp are transacted. When the hides are brought into the warehouse, they are carefully examined, and the descriptions entered in a catalogue. Such is the confidence placed in these descriptions that foreign buyers frequently place orders without examining the hides. These orders are addressed to the official brokers, and turned over by them to the hide dealers or commission houses. The market is entirely open, no reservations being made. Auction sales are held only when the market is overstocked.

English Oak Bark Extract. *Leather Trades Review,* June 5, 1912. The general opinion in England rates oak bark, in conjunction with valonia, as the best material for the manufacture of sole leather. In spite of this, the use of oak bark is diminishing. The writer suggests that extract plants be established in regions where the bark is grown, and oak trees planted to keep up the supply of bark. The transportation cost for the tanning material would thus be reduced, which might result in checking the decrease in the use of oak as a tanning material.

Tannin and the Synthesis of Similar Substances. E. FISCHER and K. FREUDENBERG. *Ber.*, 1912, 45, 915-935. Carefully purified tannin (gallotannic acid) when hydrolyzed with 5 per cent. sulphuric acid was found to yield over 90 per cent. of its weight of gallic acid and 7-8 per cent. of dextrose; the actual amount of dextrose produced was somewhat higher, for control experiments with mixtures of gallic acid and dextrose showed that losses of both compounds occur. The yield of dextrose is much too small for an ordinary glucoside of gallic or digallic acid, and the authors consider it probable that the sugar is in ester-like combination. A compound of 1 mol. of dextrose with 5 mols. of digallic acid, viz., pentadigalloyl-dextrose, $C_6H_7O_6[C_6H_2(OH)_3.CO.O.C_6H_2(OH)_2.CO]_5$, would yield on hydrolysis 100 per cent. of its weight of gallic acid and 10.6 per cent. of dextrose. This constitution is in fair accord with published results on the optical activity, molecular weight, and weak acidity of tannin, and with the results obtained by the authors by the hydrolysis of tannin. Moreover, the authors have succeeded in synthesizing from gallic acid and dextrose a compound, which while not identical with tannin

Digitized by Google

possesses very similar properties. Dextrose was combined with tricarbomethoxygalloyl chloride (see *J. S. C. I.*, 1911, 1224) by shaking with a chloroform solution of the latter in presence of quinoline, and the penta-[tricarbomethoxygalloyl]-dextrose thus produced was hydrolyzed by means of alkali. In this way an artificial tannin-substance, pentagalloyldextrose, $C_{41}H_{32}O_{26}$, was obtained. This is a pale yellow substance which softens above 150° C. and decomposes at 160° C. with slow evolution of gas. (Purified tannin shows a similar behavior at a temperature about 70° C. higher.) It has a strongly astringent and bitter, but not sour taste. It is easily soluble in water, and its not too dilute solutions become turbid at 0° C. in a similar manner to those of purified tannin. It gives in aqueous solution a precipitate on addition of N/1 potassium hydroxide similar to that given by tannin. A 1 per cent. aqueous solution precipitates gelatin solution just about as strongly as tannin does at the same concentration. If a 20 per cent. alcoholic solution be treated with an equal volume of a 10 per cent. alcoholic solution of arsenic acid, the liquid sets to a stiff jelly in a few seconds; with tannin, according to Walden, the same phenomenon is observed in a solution of about half the concentration mentioned. Its solubility in organic solvents is similar to that of tannin, except that it is much more easily soluble than the latter in warm ether. It gives a color reaction with ferric chloride and precipitates with pyridine, brucine, quinine acetate, and quinoline acetate. Its acidity appears to be somewhat greater than that of tannin. Analogous compounds have also been prepared with *p*-hydroxybenzoic acid in place of gallic acid and with *a*-methylglucoside and glycerol in place of dextrose. The work is being continued and the methods of synthesis described promise to be fruitful with respect to the constitution not only of gallotannic acid but also of other tannins. It is mentioned that the single crystalline tannin, chebulinic acid from myrobalans, also yields dextrose on hydrolysis with sulphuric acid.—A. S. in *J. S. C. I.*

Use of Tannin Materials, and Their Analysis from the Dyer's Standpoint. G. E. KNOWLES. *J. Soc. Dyers and Colorists*, 1912, 28, 174-176, through *Leather World*. For the analysis of tannin materials, the leather chemist uses either the Loewenthal or the I. A. L. T. C. methods. From the standpoint of the dyer, the weak point of both methods is the fact that hide or gelatine is used to precipitate the tannin, whereas in practice the tannin is absorbed by cotton or silk. Some experiments are here described demonstrating this difference.

Various tannin materials were analyzed, and solutions of them were made up so as to contain equal amounts of actual tannin. Pieces of bleached cotton cloth, weighing 4 grams, were placed in each for 12 hours. At the end of this time, the pieces of cloth were taken out, rinsed, and all saddened with a solution of ferric sulphate, being finally well washed, and dried.

The results obtained proved conclusively that cotton behaves in a differ-

Digitized by Google

ent manner towards tannin materials to hide, sumach and chestnut especially showing a wide divergence in the depth of shade.

It was further noticed that on comparing the density of the grey color, produced on the cloth saddened by ferric sulphate, that the depth of shade corresponds in every case with the amount of iron fixed. Sumac fixes more than six times as much iron as valonia, and about three times as much as chestnut.

Two theories may account for this: (1) either the cloth absorbs different amounts of tannin from different extracts, or (2) the tannins fix varying amounts of iron. Experiments carried out on the percentage of tannin absorbed from different extracts lead the author to state that both theories are correct, that is (1) that the cotton apparently has a selective action on different tannins, absorbing more of some than of others; and (2) that different tannins fix a quantity of iron varying with the particular kind of material.

On summarizing his results, the author states: (*a*) Where a dyer desires the greatest fixing power for least money, he must use the so-called pyrogallol series of tans, *i. e.*, nut galls, gallotannic acid, sumach, or myrobalans; and (*b*) where a dyer requires weight from the tannin material employed, he will get more value by using chestnut, valonia, or oakwood extracts, as he requires to fix a larger amount of tan on the cotton in order to combine with the proper amount of iron required to dye with logwood or other material afterwards.

The Salting of Hides and Skins. (Address.) J. PAESSLER. *Ledertechn. Rundschau*, **1912**, 137-41. The aim in preserving hides is to prevent putrefaction. The preliminary precautions are: clean slaughter-floors, each hide being collected in a separate basket. After cooling, the preserving should be carried out immediately, in any case the same day. The action of salt is (1) dehydrating, withdrawing blood, etc., (2) antiseptic. So much should be used as to remain partly undissolved on bundling. The hides should be so spread that the brine may flow off without collecting in pockets. Previously used salt should never be employed. The room should be cool to guard against putrefaction.

In spite of these precautions, the so-called salt-spots may result. Their origin is not fully understood but the speaker regards them as due to the action of special micro-organisms and not the result of ordinary putrefaction. They appear to originate on the flesh and to gradually penetrate to the grain where they are most frequent in the softer parts, neck, sides, etc. They produce in the white pelt a roughness of the grain resembling a coating with bran. In tanning, the spots darken, the surface dull and brittle; such hides are unusable for grain leather.

At the instance of the Central Union of the German Leather Industry, researches have lately been made at the Freiberg Versuchsanstalt bearing upon this subject. It had been previously observed in practice that the spots varied according as soda or petroleum was used for denaturing

Digitized by Google

the salt employed. (In passing, the speaker repeats his former advice, that alum be never used for this purpose.) Accordingly four forms of salt were used: rock salt and brine salt ("boiled" salt, Siedesalz), each denatured both ways. A large part of the hides produced in the Freiberg slaughter house during the unusually hot months of July, Aug., Sept., 1911, were daily collected, equally divided and salted with the four sorts of salt. The bundled hides were stored for 1½-4 months in cool rooms and the calf skins then made into boxcalf by Carl Freudenberg, Weinheim; the hides were tanned at the leather school, being yet unfinished. The boxcalf leather was carefully sorted with the following results:

	No. of skins	Without spots		Traces of spots		Light spots		Marked spots	
		No.	Per ct.	No.	Per ct.	No.	Per ct.	No.	Per ct.
Petrol. rock salt	107	56	52.3	26	24.3	14	13.1	11	10.3
Soda rock salt	117	99	84.6	8	6.8	9	7.7	1	0.8
Petrol. brine salt	111	98	88.2	10	9.0	2	1.8	1	0.9
Soda brine salt	117	108	92.3	9	7.7	—	—	—	—

It appears that the best results are with brine salt and with soda as denaturing agent. The soda perhaps retards the growth of the micro-organisms conjectured to cause the spots; this question is being investigated. The brine salt was coarser grained than the rock salt in all cases. All the salt was very pure. W. J. K.

PATENTS.

Process of Deliming Hides and Skins. British Patent No. 3,140. C. H. BOEHRINGER, Germany. A small quantity of a salt of an organic acid is used, with a cheap inorganic acid. Instead of 1 lb. of 43.5 per cent. lactic acid for deliming 100 lbs. of hides, ½ lb. of 50 per cent. sodium lactate may be used, with 9 oz. of hydrochloric acid of 20° Bé.

Purification of Water and Sewage by Ozone. British Patent No. 3,250. M. P. OTTO, Paris.

Manufacture of Lactic Acid. British Patent No. 2,507. O. FRIEDBERGER, Germany. Dextrose is fermented by the action of bacillus Delbrucki which has been cultivated in maltose and then accustomed to dextrose by gradually adding a solution of it to the culture. The bacillus is then added to dextrose solution obtained from grape sugar or potato starch, which has been sterilized and cooled to 120° F., and to which chalk has been added to take up the lactic acid. The fermentation is completed by the addition of bacillus bulgaricus and bacillus acidi lactici. Peptone, etc., may be added as food for the bacilli. The fermented liquor is concentrated *in vacuo*. and the calcium lactate is decomposed by the addition of sulphuric acid.

Digitized by Google

Tanning. U. S. Patent No. 1,028,563. JOSEPH FORSTER, Warrington, England. The vats are so arranged on a slope that the liquor may flow by gravity from one to the next throughout the series. Thus the hides must be moved from the vats containing the weaker liquors to those containing the stronger ones. It would seem to the lay mind to be cheaper to let the hides lie and pump the liquors!

Evaporating Apparatus. U. S. Patents Nos. 1,028,737 and 1,028,738. PAUL KESTNER, Lille, France.

Evaporating Apparatus. U. S. Patent No. 1,028,777. JOHN A. POWER, Babylon, N. Y.

Evaporating Apparatus. U. S. Patent No. 1,028,792. T. F. SANBORN, Ensenada, P. R.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII AUGUST, 1912 No. 8

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

CHANGE OF ADDRESS.

Erwin F. Cords to 1314 State St., Milwaukee, Wis.

NOTE ON THE PROVISIONAL METHOD FOR COLOR VALUATION OF TANNING MATERIALS.

By Roy H. Wisdom.

At the time of its inception in 1910, the Provisional Method for Color Valuation of Tanning Materials was suggested in conjunction with the regular skiver test when the chemist reported on the various tanning materials, in order to give those interested a line on what might be expected with a cloth test.

Digitized by Google

Evidently this suggestion was never generally carried out for recent tests made in this laboratory seem to show that not all broadcloths are alike in character and instead of approximating a closer uniformity than with the regular skiver, widely different shades were obtained with the same tanning material on broadcloths purchased from different sources.

This very point was brought up by Mr. Veitch at the time the report on this method was read, in which he said, "Now there is one point I have thought of since Mr. Kerr commenced to read his paper and that is it seems to me there is some doubt about whether different samples of wool cloth will always give the same color. It may be that we will have some difficulty in getting the same color on different lots of wool cloth. Wools grown in different sections of the country behave in different ways with dyeing materials, I believe is the opinion of dyers, and it may be we would want to look a little into that before expressing too definite an opinion on the subject. It seems to me though it may have a value."

Mr. Kerr's reply to this was as follows, "With reference to Mr. Veitch's observations, wool cloth I find comes in bolts of fifty yards, and that will cut up enough samples to standardize all the samples used in twelve months by all the chemists in the country, just the same as we standardize hide powder now. The wool can be distributed from a central source just the same as the hide powder is distributed."

While the writer is not conversant with the manufacture of broadcloth, the probabilities are, in addition to what Mr. Veitch has said, that different manufacturers use different chemicals in the processes of fulling and bleaching which act as a mordant on the cloth and thus produce the results referred to above.

If we are to continue this method of color testing it would seem advisable to appoint a Committee to investigate the statement in regard to non-uniformity of broadcloth for this purpose, and if corroborated, to recommend some such solution of the question as suggested by Mr. Kerr.

Digitized by Google

NOTE ON EXTRACT ANALYSIS.

Recently a company in the leather business determined to send samples of Chestnut Extract for analysis to three different well known chemists, members of the A. L. C. A. The samples were ten in number from ten different cars of Chestnut Extract and each sample was divided into three parts, being thoroughly shaken before dividing. The chemists were not aware that their work was being tested by comparison and a period of two months covered the analyses.

The results are interesting and illustrate remarkably close agreement, not only in the average as reported by the three chemists, but in the individual samples themselves. Below is a table showing the results of the analyses, reporting only the tannin, and giving letters A B and C instead of the chemists' names.

By studying the report you will note that A is high five times, intermediate four times and low two times; B is high two times, intermediate five times and low three times; C is high three times, intermediate two times and low six times. In one case A and C are exactly the same, which explains the total of 11 counts under A and C.

You will note that the extreme variation between the highest and lowest on the average is only eight-one-hundredths of one per cent. of tannin, while the extreme variation on one sample is sixty-eight one-hundredths of one per cent.

Sample	A	B	C
1	26.59	26.79	26.59
2	24.97	24.95	24.78
3	26.91	27.26	27.59
4	27.14	26.86	26.79
5	28.21	27.89	27.57
6	26.51	25.94	26.37
7	33.76	33.64	33.52
8	29.62	29.52	29.64
9	24.84	24.86	24.64
10	24.38	24.18	24.57
Total	272.93	271.89	272.06
Average	27.29	27.19	27.21

All this speaks well for the careful work of the chemists in question and also speaks well for the methods of analysis adopted

Digitized by Google

by the A. L. C. A. and should be satisfactory evidence to the tanner that if a sample is carefully drawn, there should be little question about the accuracy of the chemist's work.

DEVICE FOR PIPETTING DANGEROUS LIQUIDS.

Philip M. C. Armstrong.

In the JOURNAL for May there was an article describing a method of pipetting dangerous liquids. In the accompanying sketches is shown a device which the writer has used for many kinds of disagreeable liquids, including hydrochloric acid and ammonia. On account of its simplicity and portability it may be of interest. It is also useful where pipettes of large volume are to be employed, as it takes considerable lung power to fill a pipette of over 100 cc. capacity in the ordinary way, whereas by means of this device a pipette of any size may be filled without the slightest difficulty.

Take a flat bottomed flask large enough to permit of a large pipette being thrust in up to the bulb. Fit to this flask a cork, and bore in this two holes, one of slightly greater diameter than the delivery tube of the largest pipette to be employed, and the other a tight fit for a one-quarter inch glass tube. Bend this tube in such a way that it will not interfere with the free movement of the pipette, and so that it will not be necessary for the operator to look down on the top of the apparatus. If the bends are correctly spaced the operator's eyes will be exactly opposite the ring on the stem of the pipette, thus greatly facilitating the reading.

Soak the cork in paraffin to close the pores, and assemble like a wash bottle, as shown in the sketch (Fig. 1). Press the bulb of the pipette firmly against the cork, so as to make a tight joint. Now blow into the tube, and the liquid will rise in the pipette. If one breath is not sufficient to fill the pipette, place a finger over the stem to retain the contents, and take a new breath. The largest pipette may be filled in this way. The hole in the cork should be large enough to permit of the pipette being drawn out without using force. The hole may be considerably bigger than

Digitized by Google

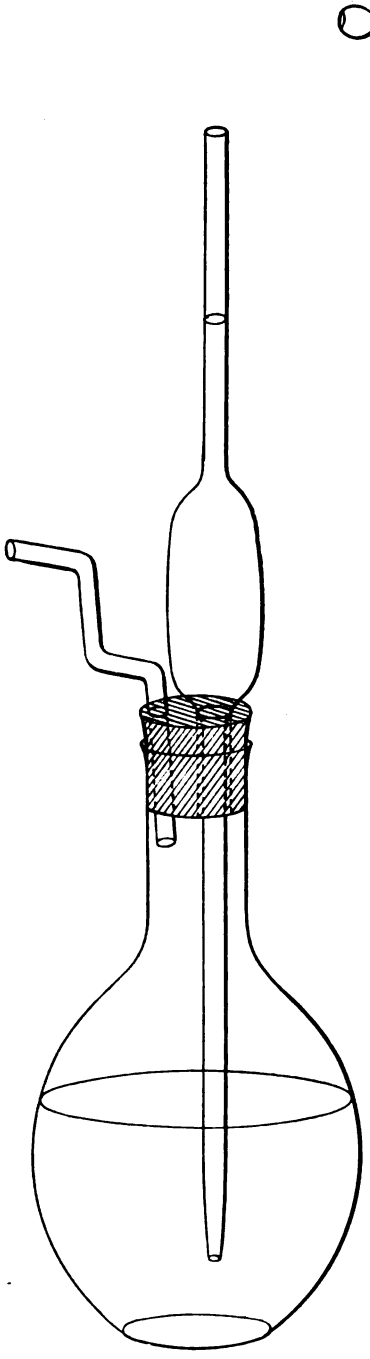


Fig. 1.

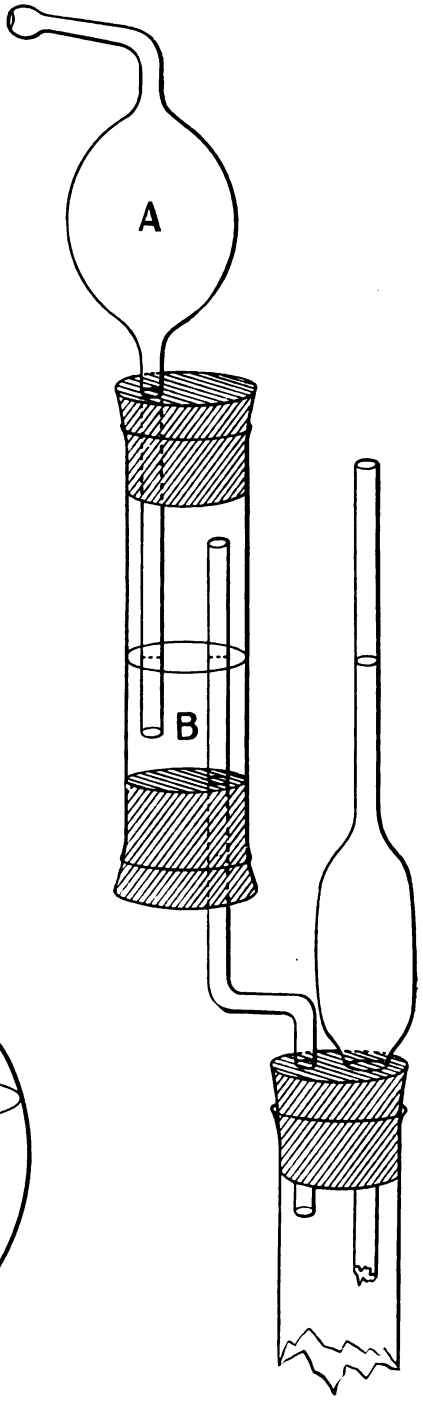


Fig. 2.—Safety trap for pipetting device. A, glass bulb to catch water in case of back pressure. B, water.

Digitized by Google

the stem of the pipette as the taper of the bulb will close it tightly when the pipette is pressed down.

When dangerous volatile corrosive liquids are to be pipetted, the safety trap shown in Fig. 2 may be profitably employed to prevent the gases from reaching the mouth. This is simply a hydrostatic seal, and can be made in a few moments from an old test tube and a couple of corks dipped in paraffin to seal the joints.

VALONIA.[1]

A VISIT TO SMYRNA AND THE VALONIA DISTRICT.

By Dr. J. Gordon Parker.

In recent years probably no material has ranked higher among the leather producing materials in the world than Valonia, and it is a matter of personal regret to the writer to see that the imports of this material have been gradually declining for some years past, as it is, I think, beyond all question one of the finest tanning materials at our disposal. Used in certain blends, Valonia probably produces a better, hard wearing, water resisting leather than almost any other material, giving weight solidity, firmness, and color to an extent which is almost impossible to obtain by the substitution of any one or number of other tanning materials.

Much has been written on Valonia, on its sophistication and on its qualities, and much of what has been written has been contradicted on the one side and re-affirmed on the other. It was, therefore, with a considerable amount of pleasure that I embraced an opportunity to visit Smyrna last Summer, and study the matter on the spot, and try to find out how much truth there was with regard to the existence of factories especially adapted to the manufacture of this natural product in the form of beard, etc., or for the grinding and preparation of sand, stones, dirt, etc., to be mixed by the wily sharper in order that dealers should be able to sell this material to English tanners delivered to the tannery at prices cheaper than the material could be bought at from the source of supply in Smyrna.

[1] Tanner's Year-Book, 1912, pp. 133-140.

Digitized by Google

After five days' pleasant sailing along the Mediterranean, one arrives at the Bay of Smyrna, and truly the sight is picturesque, as Smyrna slopes up from the quay almost immediately on landing. One gets about 200 to 300 yards of level ground, and then the town rises on all sides. The town is divided into three distinct parts: The Turkish quarter, the Greek quarter—where also live the Armenians, and the European quarter. There is no pier; and, as the water is not over deep, our liner anchors some 200 yards out in the bay. As cholera was raging and the yellow flag flying from our mainmast, the doctor and purser had to go ashore before any boats were allowed to take off passengers. On receiving our official permit, there immediately issued from every corner a galaxy of boats of all shapes and sizes, and one heard a medley of tongues of the East as the men fought to secure a passenger and his luggage.

After watching this sight for a few minutes and letting the crowd disembark, I spied a steam tug coming out from shore with the English flag proudly flying, and I was soon landed on the "Mary of Aberdeen," and shortly afterwards found myself comfortably installed in a most up-to-date European hotel, run by Germans, served by Germans, and built and owned by German capital.

Now a few words on Smyrna itself, and then to my special subject. Smyrna is a most interesting city to visit, but those doing so should either go in the early spring or late autumn, as the heat in September is rather uncomfortable for an Englishman. They should also endeavor to time their visit when cholera is not raging, as it is rather disconcerting to be in Smyrna when the death rate varies for forty to eighty per day from cholera. The drinking water is quite safe, but the sanitation is faulty. Perhaps the streets are cleaned sometimes, and occasionally they may even be repaved, but during my stay neither of these things happened. Anyone who has visited any part of the Turkish Empire will understand this state of affairs, when we remember that Smyrna is a Turkish city run by Turks, for the Turks, and in the Turkish manner. But in the European quarter the influence of European residents has made itself felt to a considerable extent, with the result that some of the suburbs such as Cordelio and

Digitized by Google

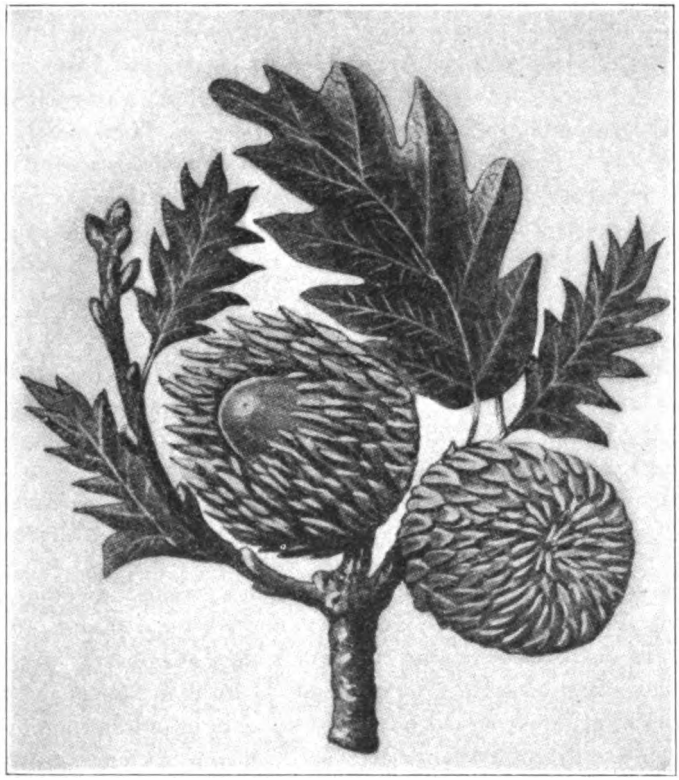
Bournabad, are perfect residential quarters. Clubs such as the Jockey Club, the Residential Club, the Yachting Club, and football, tennis and cricket, two golf courses and every other sports club exist, so that a European can at all times enjoy himself to the full. Anyone arriving with good credentials is at once received and made to feel at home, and the kindness of our compatriots in that part of the world need only be met with once to be ever remembered.

Now, to deal with Valonia. As all in the leather trade know, Valonia is the acorn cup of the Turkish oak, known as Quercus Aegilops. These trees grow in various parts of Asia Minor, some as near as sixty or seventy miles from Smyrna, larger districts at about one hundred miles away, the remainder, extending to districts as far as eight hundred miles from the port. The trees do not grow in dense forests like the English or Slavonian forests, but in clumps of a few hundred together at a distance of twenty or perhaps thirty feet apart. They grow by the side of the road, up the sides of hills, and in the peasants' grazing grounds. The trees are rather smaller than our English oak, more the size and shape of the horse chestnut. In order to visit one of these groves, you can either go a distance by train and the remainder on camel's back; or, as in my case, under most favored auspices, he whirled out in a powerful Napier motor. Needless to say the car was built for the district, or should I say for the roads? I have seen roads in various parts of the world, but the roads surrounding Smyrna deserve a special name of their own. A few hours in even the most comfortably sprung car, going at thirty to forty miles an hour is sufficient for both one's bodily comfort and nerves. It is an experience to be driven by a Greek whose one ambition appears to be to show the foreigner what speed he can get out of the car, and how near he can dodge a precipice, or a mass of rock about two feet in diameter in the middle of the road. When the so-called road comes to an end it is necessary to mount either a mule or camel, and in course of time one reaches the first grove, or clump, of Valonia trees.

The thing that strikes one first on seeing the Valonia tree is the size of the Valonia cup. It is a deep golden yellow in color, tinged with green. It is comparatively speaking soft, and about

Digitized by Google

two or three times the size of the cup as it arrives on the English market. The acorn is completely enclosed, as will be seen from the accompanying photograph. The beard grows to a length of one inch, and curls right over the acorn in close and compact form. The Valonia ripens in September, and natives from the various villages in whose territory the Valonia grows



Valonia—Quercus aegilops—(drawn from Nature).

come out and climb the trees, knocking the cups off with sticks, or pulling down the branches so that they may be picked by hand. Should the weather be fine, the Valonia is allowed to lie on the ground until the surrounding trees are harvested. It is then gathered up and taken into the village, where it is spread upon a large, flat piece of ground which has probably previously been

Digitized by Google

used for drying the sultanas. This looks like a large tennis court, and seems to be made of mud which has been baked hard in the sun. The Valonia is spread upon this to a depth of about six inches, and frequently turned over as it dries. In this drying process it loses over half its weight, and the cups contract in the drying process to about half their original size, gradually turning to the grey color so familiar to users of this material at home. In this process of turning over the beard gets separated from the cup and broken off. The acorn becomes exposed, and as the cups dry the acorn out and is separated as far as possible from the Valonia and used for feeding purposes. When partly dry, and if there is a danger of rain, the Valonia is transferred to large wooden barns, where it is piled to a depth of a foot or eighteen inches, and the drying process continued, the Valonia being constantly turned to prevent fermentation and heating, as, if this takes place to any extent, it would darken the color of the cup.

So far everything is plain sailing, but now comes the part where the Turks and Greeks excel, viz., the sampling of the crop in Smyrna, and negotiation for the price of the subsequent bulk delivery.

The peasant owner, or probably an astute middleman employed by him, arrives in Smyrna bringing samples of his crop. He arrives with his four or five camels strung together, the camels always being led by a little donkey. After rest and refreshment, he visits one after the other the Valonia dealers, displays his samples, usually asking a much higher price than he has any hope of obtaining. Then, in truly Eastern style, he wanders round from one warehouse to another, bartering, praising his wares by Allah and every other prophet, and finally, after three or four days, his crop changes hands. The customary coffee is drunk, and the deal when once made is binding. No written contracts are made, as, having passed his work and sealed his deal by a friendly cup of Mocha, no true Turk ever goes back on it.

It is at this stage that the expert buyer is of incalculable value, as he has to buy a crop of sometimes many hundreds of tons from the sample four or five bags brought in on the backs of the

Digitized by Google

camels. They are put down in an open courtyard close to the street and must be valued there and then at so many piastres per kintal. The buyer must be able to judge quality, percentage of beard, percentage of unremoved acorns, and how much sifting and ventilating this would require before being in a fit state to ship. He must be able to talk Turkish, Greek, and possibly other languages. He must not be in a hurry, and must never appear eager to buy, but be prepared to see the material packed again on the backs of the patient camels, to be led away probably to his keenest competitor.

It is here that those who have been in the Valonia trade for years have a distinct advantage, for I am strongly of the opinion that the consumer often suffers by reason of the fact that when Valonia is plentiful and prices comparatively low, many amateurs dabble in this Valonia industry, and thus they have on more than one occasion unnecessarily raised the market price, and so raised the price to the consumer.

In due course the Valonia arrives in Smyrna, and is taken into one of the huge warehouses, where it is carefully weighed and tipped into large bins prepared for it, each crop from each separate district being kept distinct. As it arrives still containing an excess of moisture, it has to be again turned over frequently to prevent heating.

Many years ago Valonia was stored and encouraged to heat. This process improved the color. It was formerly laid in great piles ten to fifteen feet deep, and allowed to lie until it steamed and the top layer turned black to the depth of a foot or so. This was taken off, and the remainder was then turned over and cooled. This process, however, was found to damage the Valonia, in addition to which, the top two feet or so which turned black was wasted. It was further found to deteriorate the tanning qualities.

Now comes the sorting of the Valonia into qualities. For this purpose numbers of women and children are employed to pick over the Valonia, the finest cups being shipped to Russia and Trieste, the second quality to Norway, Sweden, Austria and Germany, the third, or refuse, being known as Eglise, or English quality. In this picking over, acorns, pieces of twig, stones and

Digitized by Google

leaves are all sorted out. The material, when properly graded together with its proper percentage of beard, is now packed ready for shipment, under the various marks, indicating qualities.

We in England, as a general rule, know little or nothing of the different growths and qualities which exist. We have been accustomed to buy largely on appearance, and there has been a general tendency to beat down the price. I maintain that in this the English buyers have been wrong, and I believe that the Russians and Germans get better value for their money than we do, as this constant depression of price has had the effect of creating methods of blending to suit the price, and this blending has undoubtedly deteriorated the material as a tanning agent. It has meant that the best growths coming from the finest districts of Asia Minor no longer find their way to the English market, and practically every parcel has to be mixed with a proportion of caramanian or ground cups. The beard is frequently removed and substituted for beard from an inferior quality mixed in with ground twigs, ground acorns, and even ground cups. However, if one deals with reliable shippers, it is certain that no deliberate adulteration takes place. I was unable to find, even after the most diligent inquiry, that any factories existed for grinding sand or any Valonia substitute, but among some of the smaller dealers there certainly exists a method by which small acorns and inferior cups are ground up to substitute the beard, or to mix with it, and I have no doubt that some of the unscrupulous middlemen have been known to mix in a certain proportion of calcareous constituents in the form of small pebbles and stone, in order to bring down the price of Valonia to that offered by the English merchant. Such customs, however, are never adopted by any of the reliable shippers who have been in this business for years, and whose reputation is above such tricks.

One thing which impressed me in September last, was the enormous demand for Valonia beard and the price paid in comparison with that for ordinary Valonia. This demand had created the supply, and there was more beard coming out of Smyrna than naturally existed. It is not difficult to draw conclusions from this. Those who had Valonia were sifting it, putting the Valonia through various so-called cleaning machines, denuding

Digitized by Google

the cups to a very large extent, in order to supply the demand. Those tanners, therefore, who bought ordinary Valonia most have suffered in two ways: (1) By receiving deliveries of Valonia with a less proportion of beard than should have been naturally present; (2), By having the quantity of beard made up, either by the blending of Greek beard or by the blending of ground twigs, and ground immature cups.

I do not by any means profess to be an expert on Valonia, but I spent a most interesting time in trying to become acquainted with the various growths and qualities; and my instructors, even after several days' patient coaching, were able to do me every time; and I have come to the conclusion that no tanner in this country is able to judge a delivery of Valonia to within 10s. a ton, that is if the shipper prepares the Valonia. By a screening and cleansing process the Valonia may be made to look bright in color. By putting it through a process of sifting and shaking, it may easily be made to look 10s. a ton better, and without a most careful examination of the beard with a powerful magnifying glass it is impossible to tell whether the beard is actually beard or a mixture of beard and other materials; and I cannot help thinking that it would have paid, and would still pay, the English tanner to give a better price for this material than he has hitherto done, and only buy through reliable shippers a guaranteed quality, unmixed and unsophisticated; by which I am sure he will obtain both better weights and better leather. It would pay him to study the different districts where the Valonia grows, and the different qualities which each district produces. One district produces a larger cup than another, or it may be a different shaped cup. From one district one gets a Valonia which produces heavy bloom and tans comparatively slowly, from another a Valonia which gives little bloom but tans rapidly. Some Valonia produces a dark cut to the leather, while others produce a leather of a light shade, everything depending upon the district and the soil. The German and Russian tanners have studied this question, and, as they still continue to buy these special qualities, it makes one think they know more about the subject than perhaps we do.

The average crop of Smyrna Valonia is about 70,000 tons a

Digitized by Google

year. The last harvest only yielded 32,000 tons. This shortage was due to cold easterly winds and frosts in the early spring, the trees only bearing fruit on one side, the side exposed to the north and east wind being completely bare of cups. Each tree is supposed to bear from four to six hundred-weight. In very good seasons this may in some cases run to eight hundred-weight. The best districts for quality are the following: Nasli, Gundai, Borlo, Demirgick. Three very poor districts are Ushack, Ghediz, and Barnas. Marin and Mitylene, on the coast of the island, grow good varieties. The Caramanian Valonia seldom averages more than 25 per cent. of tannin, compared with 38 per cent. of Nasli. The leaf of the Caramanian is different to the ordinary, and the fruit is easily recognizable by its sharp pointed beard.

In passing, I might mention that I have been supplied with large bulk samples of all the different growths and qualities. It is my intention to carry out a careful series of investigations with these, but large samples have been placed in our College Museum, where they may be examined at any time by any of our readers.

In Smyrna, there are two Valonia extract factories, where the Valonia is extracted and manufactured into dry powder. I was privileged to inspect one of these factories. It is solidly built of stone, and fitted up with latest up-to-date plant for the manufacture of extract. I have visited extract factories in all parts of the world, but confess that I have never seen a factory so splendidly arranged with every labor saving device and with every requisite for the manufacture of extract on scientific lines. The Valonia cup and beard, on arrival at the factory, is carefully sifted, and every trace of iron and extraneous matter removed by sifting and passing over an electric magnet. After grinding, the Valonia is extracted at a moderate temperature, the liquor is immediately concentrated to the consistency of syrup, and subsequently by a patent process devised by a member of the firm, transformed in two minutes into a perfectly dry powder containing a maximum of 4 per cent. of moisture. No chemicals are employed, and there is no bleaching, and a delivery of Valonia may go into the factory at 10 o'clock in the morning, and by the same hour in the evening the extract from it is bagged ready

Digitized by Google

for export. It will readily be seen that with a process as rapid as this the natural qualities of Valonia are not impaired. There is no time for decomposition or fermentation. Therefore, the Valex, or dry Valonia powder, as would be expected, has been proved to possess all the special qualities of the material from which it is made.

One may say that it is not a manufactured product: it is simply the Valonia prepared in the most convenient form for use in the tanyard. I was permitted to visit this factory on various occasions, and saw the store of Valonia waiting to be made up into powder and was struck with the quality. The Eglise variety is not employed being considered too poor. Only good qualities of Valonia and beard are used, otherwise the color and strength suffer materially. The assurance and verification of the fact that manufacturers of this extract cannot and do not use such poor quality of Valonia as is shipped daily to the English consumer, suggests the following questions:—Is the English consumer as wise as the Valonia extract manufacturer and continental competitors? Is the English Valonia buyer able to judge the value of Valonia solely by appearances? Can the best results be got in English tanneries from Valonia that is usually a blend of the refuse of all districts? Would it not pay all users to get into direct touch with shippers and try some deliveries from specific districts, watch the results, and so be able to answer these questions for themselves?

I desire here to express my sincere thanks to the members of the firms of C. Whittall & Co. and Barry Bros. for their many kindnesses in placing facilities at my disposal for seeing everything described above, for reliable information, and for the authentic samples of the various growths which they have kindly collected and sent for the purpose of further study.

RISING OR PICKLING OF SKINS.[1]

By J. T. Wood.

The origin of "rising" or "raising," and also the etymology of the word, lies in very early observations of the swelling or raising action on skin of fermented infusions of bran and meal.

[1] Tanners' Year-Book, 1912, pp. 116-118.

Digitized by Google

When this fermentation is conducted in a proper way, considerable amounts of acid are produced (1), and skins which have been properly freed from lime, when placed in such solutions, swell considerably (2).

It is not known who first observed that this swelling is repressed by immersing the skins in a strong salt solution, but it is evident that after McBride's invention of the application of sulphuric acid to the swelling of skins (2) that the step to the modern method was a comparatively simple one. The date of this may be approximately fixed as between 1780 and 1800.

The early method of "rising" consisted in stirring the skins in a solution of sulphuric acid in water (3); the strength of the solution was about 1-300. In this solution the skins become swollen and gelatinous, and can be easily penetrated by the fingers. After twenty minutes they are transferred to a solution of salt S.G. 1.065, in which they are stirred continually, until the swelling is reduced, and the skin assumes a white appearance and is "leathered." This takes about twenty minutes. The skins are then placed in a saturated brine, in which they fall completely. After one hour in this brine they may be drained and packed away. They will keep indefinitely in this state, and are a kind of leather. The workman, in fact, determines if the skin is properly "rose" by pinching a fold of it between finger and thumb, when, if properly pickled, it shows a white streak like alum leather. In the modern method of rising the skins are introduced directly into a solution containing $^{50}/_{60}$ grams of common salt, and $^{4}/_{5}$ grams of strong sulphuric acid per litre. The usual solution is in fact decinormal. In this they are paddled forty to fifty minutes, when the acidity diminishes to 40 cc. N/1 per 100 cc. They are afterwards transferred to saturated brine, as above described.

The following table shows the course of the pickling process in practice.

It gives the absorption of acid in a series of goods put through the same paddle and strengthened up for each successive lot of skins. The salt was kept constant at 12 degrees Tw. (1.060 S.G.) The weight of dry pelt per litre of solution was approximately 100 grams.

Digitized by Google

Lots of skins put through	Cc. N/1 alk. per 100 cc. Before goods	Cc. N/1 alk. per 100 cc. After goods	Acid absorbed
1	11.4	4.5	6.5
2	11.7	3.3	8.4
3	10.3	3.6	6.7
4	10.2	5.7	4.5
5	13.4	4.1	9.3
6	11.2	2.4	8.8
7	9.1	4.4	4.7
8	10.8	4.9	5.9
9	12.0	4.4	7.8
Mean	11.1	4.14	6.94

Procter, who has studied the process very thoroughly, points out that skins may be effectively pickled with very much smaller quantities of acid than those ordinarily used. The skins are first put into a saturated brine bath, and then a calculated quantity of acid added, not exceeding 0.1 gram molecule of sulphuric acid per kilo of dry hide substance(about 100 gram acid per 100 kilos wet skin or about 1½ ounces acid per 100 pounds wet skin). In this case the whole of the acid is absorbed. The solution must then be brought up to saturation by addition of solid salt, as the skins part with a great deal of water in the bath. This method is interesting as showing that the acid in the rising bath could in many cases be reduced with advantage, though more time would be required.

Stiasny and Eitner (9) have made a number of important experiments on pickling, for particulars of which the original article should be consulted. The conclusions to be drawn from their results are as follows:—

1. The amount of salt taken up by the skins does not depend on the nature or strength of the acid present, but is proportional to the concentration of the salt in the pickling bath.

2. The amount of sulphuric acid taken up by the skins is not proportional to the amount present in the pickling bath, but is a diminishing quantity, that is, the absorption is of a similar character to the absorption of tannin by skin.

Digitized by Google

3. The amount of acid absorbed appears to be practically independent of the amount of salt present.[1]

4. Different acids are taken up by the skin in varying amounts.[1]

Pickled skins must not be brought into contact with water; a drop of water accidentally sprinkled on the skins will eventually induce putrefaction, which then frequently spreads to other parts of the skin in a very extraordinary way. It certainly seems strange that putrefaction should take place in the presence of N/10 sulphuric acid, and a large quantity of salt, but the writer has found both moulds and bacteria capable of growing in such solutions, and as soon as a growth is established, the acid is quickly neutralized by ammonia compounds produced by the bacteria, after which putrefaction pursues its normal course (5).

Many other acids have been tried for pickling, but none have hitherto proved so good and simple in practice as sulphuric acid. In 1904 Mr. Seymour Jones (6) at the suggestion of Professor Procter, carried out some experiments on the use of formic and acetic acids as pickling agents. The skins were paddled in a 0.25 per cent. solution of formic acid at 70 degrees F., and left in the acid solution for twenty-four hours. They were then paddled in a saturated solution of common salt, and left in this for twenty-four hours. The color and appearance were equal to an ordinary pickled skin. These skins were afterwards sent up the Amazon river to Manaos, and back to England—a severe test—and were found to be in perfect condition on their arrival in England. They tanned well and conformed in every way to the conditions laid down in the Society of Arts Report on Leather for Book-binding (7). Acetic acid in solution of 0.1 to 0.2 per cent. was found to be equally efficient, and somewhat cheaper. In the writer's opinion the solutions used by Mr. Seymour Jones are too weak. Solutions containing at least 0.5 per cent. formic acid ($H.COOH$) should be used. This amount equals 5.2 to 5.5 gram per litre of 90 per cent. acid; and gives about an N/10 solution. In this case the operation of rising may be carried out exactly as with sulphuric acid, and takes no longer time.

[1] Professor H. R. Procter remarks with reference to: (3) Addition of salt increases the acid actually fixed up to a given maximum, but diminishes the volume of solution absorbed. (4) Only partially true, the acids are absorbed in molecular proportion, though some deviation from this occurs.

Digitized by Google

Where time is no consideration, Mr. Jones' method is of course cheaper, and the amount of formic acid used appears to be sufficient to preserve the skins. In the case of other organic acids, so far as I am aware, it has not been shown for how long they will preserve the skins.

In conclusion, it may be noted that there is a loss of skin substance by solution in all "rising" processes. The amount of skin dissolved depending upon various conditions. In a case investigated by the author, the amount of skin substance found in the rising liquor was 2.9 grams per liter, or 3.5 per cent. on the dry weight of skin put through.

The estimation of the skin substance and general control of rising liquors is at present under investigation by a commission appointed by the I. A. L. T. C., of which Dr. Gordon Parker and the author are acting as referees.

REFERENCES.

(1) Wood & Wilcox, J. C. S. I., 1893, p. 422.
(2) Art of Tanning and Currying Leather, etc.; also the new method of tanning invented by David McBride, M.D., 1780.
(3) J. T. Wood, Jour. Soc. Chem. Ind., 1898, p. 1,011.
(4) H. R. Procter, Principles of Leather Manufacture, p. 90.
(5) J. T. Wood, J.S.C.I., 1906, p. 109, 1910, p. 665.
(6) A. Seymour-Jones, Collegium, 1904, p. 186.
(7) Society of Arts, Report on Leather for Bookbinding, 1905.
(8) Stiasny & Eitner, Studie über den Pickel, Der Gerber, 1905, p. 125, etc.

THE MANUFACTURE OF BELTING BUTTS.[1]

By G. B. Stockton.

There is probably no leather manufactured which has to stand such severe strain as belting leathers, as the high speed at which machinery is being run to-day demands the very best in belting leathers, if it is to prove satisfactory, and last for any length

[1] *Leather World*, IV, 435-6, 479, 495-5.

Digitized by Google

of time. In opening my subject, therefore, I may say I believe the day of common belting, manufactured from inferior hides, tanned with cheapest materials, and weighted up to the hilt in the dressing process, is almost over. Butts thus manufactured have been weighed in the balances and found wanting, and the man who has to pay realizes that the low priced article is both inferior and more expensive in the long run.

There is no doubt that the method of selling by weight has led up to the ridiculous competition manufacturers have entered into; but I think there are not signs wanting that the fittest will eventually survive in the matter of belting. I have noticed also several advertisements of late appearing in this journal for experienced curriers to hand dress these goods. I am not altogether surprised at this; for whilst I fully advocate a scouring and setting machine, there are other processes through which some of our more modern belting pass, that to my mind are detrimental to the production of a high class butt, and which in the course of my article I shall refer to.

Selection of Suitable Hides.

It will be quite obvious to all, that best butts cannot be produced from inferior hides; therefore, it is necessary to select those hides in their raw state that can reasonably be expected to give best results in the finished leather. In the first place I cannot recommend dry imported hides, or those that reach us in a more flaccid condition. The best for the purpose are fresh (not salted) English hides. A bull hide has the advantage that it runs out better to the shoulder and belly than any other class of hide, but the disadvantage is found in its inclination to be stretchy in wear, owing to its fibrous and loose structure of pelt. I am aware there are large quantities of belting leather made from these hides; I may also say that if the bull hide is properly treated in the tannery, and passed under the roller *before* receiving any grease, the looseness and stretch are a good deal obviated. However, the best hides for belting are ox and heifer, and although netither of these run out to anything like the substance of the bull hide in the shoulders and bellies, they are finer and closer in pelt.

The first process is to, of course, soak the hides in a pit of

Digitized by Google

clean water to remove the blood, and to wash the hair as free as possible from adhering dung; 24 hours will be sufficient for fresh hides. The hides are then drawn, when they will be ready for the lining process.

Good Liming Essential.

The liming of hides is a simple process from the practical side, however complex it may be from the scientific one. The chief points in my opinion to be observed are the requisite quantity of good lime, properly prepared and cooled before use, and a systematic handling of the hides. I do not know of any material difference in this process beyond, perhaps, accelerating the process by the addition of sulphide of sodium.

Liming is, in some yards, performed in a single pit, but for belting and sole leathers it is not so satisfactorily accomplished, as for leathers for other purposes.

The method I shall advance is what is known as the shift or three-pit system of liming. In this way a more uniform and better liming take place, the goods going into lime liquors of gradually increasing strength, and finishing off with a fresh new lime.

The hides are placed first into the backward lime pit, which is mellowed down from the fact that two lots of hides have previously passed through. This backward pit, therefore, contains bacteria which immediately attack the structure of the hide and hair sheaths, and thus loosens the hair at the roots. Then, as the hide plumps up in the stronger lime, the hair becomes quite loose, and is easily removed with a blunt tool. This backward lime pit, however, has little plumping effect but rather a softening and solvent action.

The hides remain in the backward pit from four to six days, the time being regulated according to the condition of the hide and the time of the year. During summer months hides in this back pit must be carefully watched, to prevent injury to the pelt. Much hide substance can be lost in this way which will not only mean a loss of weight on the finished leather, but will prove otherwise detrimental to its quality. If this back pit become too heavily charged with solvent elements, which may easily occur

Digitized by Google

during hot weather, a good plan will be found to always keep a tub of pure milk of lime handy, ready for use. A few buckets of this added will considerably help to check the solvent action.

The hides from here pass on to another pit containing stronger liquor; this liquor further checks the bacteriological action, and has a plumping effect. A bucket or two of pure strong lime liquor added when the hides are out of the pit will also be found beneficial here.

The hides should be handled at least three times during the week they remain in this pit. A fresh new lime pit is now made up; for this use about 7 pounds of lime per hide. The pit is prepared by first putting the requisite quantity of lime into the pit, then sufficient water is run in to thoroughly slake it. After this, a further quantity of water is added, until the pit is about half full. The pit is then left over-night. Next morning the hides are drawn from pit number two, when the fresh new lime pit is well plunged, and the hides placed therein one by one, as flat as possible. The hides remain in the new lime for a week, and are drawn up twice. The hides will then be plumped up, and sufficiently hardened ready for the unhairing process.

Unhairing and Fleshing.

The method of unhairing by hand is too well known to need enlargement. At the same time, I should like to remark that, owing to the simplicity of the work, the man with most muscle and least brain has to tackle the job. It will be prudent, therefore, on the part of the man in charge to examine the unhairing tool before allowing it to be used, as much scratching and chipping of the grain might result from a coarse and sharp tool. Sharpness is not an essential for the satisfactory carrying out of this process.

The hides after unhairing are replaced in a pit of clean water, and from here are drawn one by one, and fleshed.

The fleshing of hides for belting butts is, in my opinion, very much more satisfactorily accomplished by hand labor than by machine. I need hardly remark that, to properly perform the work it requires a good deal of skill and experience, coupled with sound common sense. It used to be said this latter quali-

Digitized by Google

fication was a missing factor among fleshers, otherwise fleshers would be exceedingly rare. Be this as it may, there is a wide gulf between the man who simply removes the flesh, and rarely ever stabs the hide, and the man who removes the flesh and a good portion of the pelts as well, and who invariably stabs, into the bargain.

The chief necessity for the intelligent flesher is a keen cutting edge; therefore, it will be necessary to devote special attention to the grinding and clearing of the knife. The bevels of the knife should never be allowed to become too short; when this happens a good edge cannot be obtained, as a good, flat thin bevel is best.

A little extra time devoted to grinding and clearing the knife will well compensate the workman and his employer. Belting hides should be cleanly fleshed, as this will render much further skiving in the dressing process unnecessary.

The hides, after fleshing, are replaced usually into the water pit again, and are then scudded over on the grain side on the beam.

It is not usual to bate belting butts; they go through similar to sole butts, in a swollen condition. But 12 or 14 hours' mild bating would have a beneficial effect on the grain side, and the butts in wear would be less liable to crack.

After fleshing and scudding, the hides are ready for rounding. Rounding is not difficult to perform, but it needs a good deal of care to get in the right place when removing the bellies. It is usual, when taking off the shoulder, to cut the butt to the proper length, generally from 4 feet 6 inches, to 5 feet, butts being rarely left longer than this latter measurement.

The Tanning Operation.

At the outset of the tanning process, this question presents itself: What results are the materials selected for use likely to have on the pelt under treatment? To satisfactorily answer this question, one has to know something of the effect that each material has singly and in combination. This knowledge requires intelligent practical experience under actual manufacturing conditions, and is the principal factor for the practical tanner. This being so, it becomes necessary in order to obtain the best re-

Digitized by Google

sults, to select those materials likely to produce the effect required, employed singly or in combination, increasing degrees of strength. A belting butt cannot be tanned like a dressing hide, on the one hand, nor as firm as sole leather, on the other. Yet, firmness is an essential qualification, combined with a limited amount of pliability for belting. A butt of this description will be the result of the following method of tanning: On entering the tannery the butts are first suspended in a weak, mellow and acid liquor. The liquors are brought down to this mellow condition, from the fact that previous lots of butts have passed through, and absorbed the more astringent tannin. They remain in this first suspender three days, and are handled as frequently as possible; the fourth day they are moved forward into a little stronger liquor, where they remain another three days with frequent handling.

The butts in this way pass through six suspender pits, in liquors of increasing strength, varying from 2 to 14 degrees Bk. They are always best suspended, as this has a decided advantage over the old method of laying flat in the pit, a finer grain and better color being obtained. I may also remark that should the liquors in the first suspenders be at any time too sweet, one quart of lactic acid added to the liquors will prove beneficial. I may further remark my method, which I think is the usual one, is to pump off the most backward suspender liquor, and make up with a new fresh one. The materials used are a clear liquor of oak bark, made up in the leach, and pumped into the suspender. Then two buckets of gambier liquor—about nine gallons— and one bucket of quebracho—from four to five gallons—are added, to the bark liquors. The pit is well plunged, and the butts have eight or ten days in this liquor, with occasional handlings. The time alloted the butts altogether in the suspender is about five weeks.

Oak bark liquor is undoubtedly one of the finest tannins procurable for these goods. It is not a harsh, hard tanning agent, and, used as above mentioned, imparts scarcely any bloom. Gambier is about the softest and most mellow of all vegetable tannins, and is largely used in early liquors. It has a reputation for plumping and keeping the fibers of the pelt open, thus allowing a

Digitized by Google

larger amount of the more astringent tannins to be taken by the pelt subsequently.

Quebracho can, I think, scarcely be considered a good tanning material in itself. However, there seems some diversity of opinion as to how it behaves in use, but if used in a subordinate position, as above indicated, with the other two materials, it becomes useful and accelerates the process in the suspenders.

Having passed through the suspenders, the butts are shifted forward to be further treated in a round of dusters. These pits contain liquors of increasing strength from 15 degrees to 25 degrees Bk. And in addition to the materials already mentioned, oak bark and myrobalans are used, both materials being ground up together in the proportion of 1 ton of bark and 5 hundred weight of myrabolams.

The shifting of the butts from one pit to the other into stronger liquors is, in some yards, very irregularly done. This is a mistake. However, the shifting must be left to the tanner himself, as he knows how best to work his own round. But I should like to point out that it is unnecessary to allow leather to remain too long in the same strength liquors, and I think this was one of the fallacies of our forefathers. To illustrate what I mean: suppose butts having been lying in liquors of 20 degrees strength, are shifted forward into liquors of the same strength, in my opinion the tanning would proceed very slowly; but if the leather is put forward into liquors of 25 degrees the tanning will satisfactorily proceed. Therefore it is necessary to carefully watch and test the strength of liquors each time, and in each pit as the butts are drawn.

In some yards the butts are shifted once a week; in others twice. I recommend the last named. When a shift is made, the pit containing the weakest liquor in the round is pumped away into one of the leaches, and is refilled with a liquor of suitable strength. The most forward pack in the round is then put into this new liquor and a liberal dusting of oak bark and myrobalans is laid between each butt—preferably on the flesh side. This new liquor should be about 25 degrees Bk. The butts remain in this round of pits about two months, when they are moved forward into another round of layers.

Digitized by Google

For the making up of a new layer—in addition to the stronger liquors pumped from the leach—a dusting of 60 per cent. oak bark, 25 per cent. myrabolams and 15 per cent. of valonia, are ground up together, distributing the myrobalans and valonia as evenly as possible amongst the bark when grinding. The density of our finishing-off liquors are from 35 degrees to 40 degrees Bk. Valonia and myrobalans are two well-known and largely used materials, both of which belong to the bloom-giving group of tannins. They possess filling and firming properties, which are essentials for belting leathers.

The butts, I may say, remain in the layers about ten weeks, making a tannage of about six months altogether.

The tanning completed, the butts are drawn up and washed so as to remove any particles of adhering bark, after which they are brought to the machine and scoured on the grain side. They are then horsed over night, and hoisted into the shed, oiled lightly on the grain with cod-oil, then hung up and dried out slowly. When dry the butts are taken down and are ready for the dressing process.

Skiving the Butts.

Previous to being skived—should this operation be at all necessary—the butts are split down the back. A straight edge is very useful, laying it along the center of the butt, from neck to tail, then marking a straight line. This will ensure a straight cut and minimize loss when straightening, previous to cutting into strips when the belt comes to be made up. After splitting the butts are fellow marked, then weighed, either singly or in lots. The number and weights are then entered into the stock book, then they are passed on to the curriers to dress.

Hints on Currying.

First of all the butts are soaked in tepid water, and if found necessary they are skived. This work is best done on the table with a whitening sleaker. Of course, if the butts have been cleanly and properly fleshed no skiving is needed. But it is not an uncommon occurrence, when one has to buy butts from the tanner, to find a good deal of flesh left on the butts; in this

Digitized by Google

case the currier must resort to skiving, otherwise they will, after setting, present a pitty appearance.

The butts on coming into the scouring house are put into tepid water, and are then thrown on to the scouring slab flesh up. Give this side a thorough good sleaking with a sharp stout sleaker, then brush up with a stiff brush and give another sleaking. Go over all the butts in this way, then replace in the water and begin on the grain side by first giving a stoning. Cover the grain side again with water, and pick out any little patches of bloom the machine failed to remove with a fine piece of pumice stone. Give a good brushing and sleak off, when they are ready for sumaching.

Sumaching and Stuffing.

For belting butts a good sumaching is beneficial as it has a softening effect, which materially obviates the risk of cracking grain and also bleaches. Care, however, is necessary not to place the butts in too hot liquors. The quantity of sumach I use is 2 pounds to each butt. The usual method is to place the quantity of sumach into a suitable vat with sufficient clear liquor or water, and boil up by means of steam pipe. Then cool down and place the butts in the liquor, handling a couple of times. They should be left in the liquor until thoroughly cooled, then rinsed through clean water and allowed to drain. Then take to the shed, punch holes both sides of the neck end, and hang up to sam ready for the stuffiing process.

This is the most important process in the dressing of strap butts; it is the process that chiefly fixes the price, and which has for years made competition what it is to-day in the selling of these goods. Still, buyers are no longer in the dark in regard to the reason why cheap butts are made from dear hides. I am further convinced that it only needs a little more educating of the buyer and a guarantee from the manufacturers that their production is absolutely free from adulterants to obtain a price that will leave a margin of profit and I am sure a most satisfied customer. There is no doubt that belting leathers have come in for a large amount of adulteration. Glucose, etc., and dip and drum methods are all employed for the sole purpose of adding weight, and reducing the price per pound.

Digitized by Google

But if either of the above methods are employed the belting is not as good in wear as a purely hand stuffed butt. Glucose, if used at all excessively, coupled with a hard tannage, are, in my opinion, the chief causes of the constant complaints of cracking and breaking belts. But probably glucose is not used so extensively for weighting as was the case a few years ago.

The dip method, that is to say, laying the butts in hot greases, if properly carried out, is to be preferred, apart from hand stuffing. The drum method I do not recommend for belting, although it may be profitably worked for shoe or even harness leathers. But tumbling butts about in a drum until they have absorbed an excessive amount of grease is detrimental for belting. Butts thus stuffed have, it is true, a good appearance and handle firm in the finished leather. In wear, however, the friction of the pulleys makes the leather soft, and the belt soon gets out of shape and gives a good deal of trouble.

The best method for stuffing butts, where an unsophisticated leather is being dressed, is the following. In the first place I would emphasize the importance of having the butt in a properly sammed condition, similar to that required for drum stuffing. Then apply a thin coat of dubbin, cod-oil and tallow (two-thirds oil, one-third tallow), to the grain side. Go over all the butts on this side first, then turn flesh up and stuff with a little stiffer dubbin. Then lay the goods in a pile and leave them for four or five days covered up. At the expiration of this time the leather will have taken up a good deal of the stuffing, although in a damp condition. Then set the butts out thoroughly on the grain side, removing all marks, and extending the butts as much as possible. Now stuff the grain side lightly with dubbin of half tallow and half oil. Hang up in the shed until in a semi-dry state, then take down and give a good pebbling and glassing on the flesh side, and hang up for a few days further drying. Then take down and pebble and glass the grain side and hang up again and dry out.

In some works the butts are finished off at this stage by simply pebbling the flesh, sleaking the grain with a dull thick sleaker, and rubbing up with flannel.

The butts should now present an excellent appearance and be

Digitized by Google

firm and of uniform color, with a dry feel. Some, however, prefer treating them with a little more grease by giving a thin coat of stiff dubbin to both flesh and grain. In this case they are allowed a month or so to take up the stuffing, and to again regulate in color. This will also necessitate a little further finishing by sleaking off the grease on both sides with a stout sleaker, then cleaning the edges and rubbing up the grain with flannel.

THE PERMUTIT SYSTEM OF WATER TREATMENT.[1]

By L. H. Harrison, M. Sc., Ph. D.

The question of water softening and of water treatment in general is attracting the attention of manufacturers more and more every day, and the long list of purification processes on the market is being constantly added to. In the field of water softening alone, for example, one can mention off-hand a dozen types of machine which are in use with more or less success in the industrial centers of this country. Practically every one of these machines works on the same fundamental chemical principle, and the variations in the systems are due merely to differences in the mode of application of the chemicals and to various more or less important changes of a purely mechanical nature. Of late years a new system has been evolved based chiefly on the work of Professor Gans, of Berlin, and it is this system, working on an absolutely new principle, which bids fair to revolutionize our modern methods of water treatment.

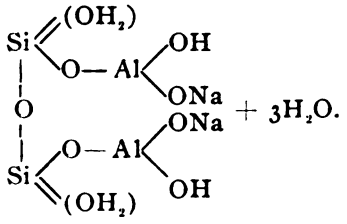
The advance of this last-named process into high favor in the industrial world has been extremely rapid, and already on the Continent some hundreds of plants are in use, while one installation alone near Bremen is treating a matter of some 3¼ millions of gallons of water per day. This popularity of the system is the more remarkable in face of the fact that only a few years ago the active chemical material known technically as Permutit was only a laboratory product.

As already explained, it is Professor Gans to whom we owe the discovery and development of the principle on which the Permutit processes are based. The Permutits, as we know them,

[1] *Chemical World*, July, 1912, I, pp. 238-240.

Digitized by Google

are all complex silicates containing as a constant constituent some proportion of aluminium. To the inorganic chemist to-day there is, perhaps, no field of study more difficult than that devoted to silicates and felspars. To deal with these substances we have to have recourse to melting processes, and the high temperatures necessary and the complexity of the constituents have together militated against much advance in our knowledge of the constitution of the silicates. Dr. Gans has recognized various classes of silicates and has invented a workable hypothesis by which he explains their chemical behavior. By melting together soda, china clay and some other ingredients in certain proportions, Dr. Gans obtained an artificial aluminium silicate which possessed properties which similar natural silicates possessed only in very minute degree. A careful comparison of the behavior of the silicates led him to the conclusion that in the natural silicates the sodium or potassium base was joined direct on to the silicic acid—the atoms of hydrogen of the latter being replaced in the usual way by metals. On the other hand the artificial product differed from this in that the base was joined on to the silicic acid through the medium of alumina. The graphic formula of a simple artificial aluminium silicate of the empirical formula $Na_2O.Al_2O_3.2SiO_2.6H_2O$, would then be somewhat as follows:



Gans named these bodies "Permutits" from the Latin root "permutare" = "to exchange," as by this name he gave expression to a most important power which they possess—namely, the property of exchanging their bases. Let us take, for example, Sodium Permutit, the most widely known of the Permutits. It contains aluminium and silica with the base sodium. If now we pour over this a solution containing calcium, the sodium is driven out by the calcium and Calcium Permutit is formed, the sodium going off in solution united to the acid radicle originally joined

Digitized by Google

on to the calcium. Conversely by acting on Calcium Permutit by a sodium salt in excess, Sodium Permutit is reformed, the calcium being expelled.

The Sodium Permutit of commerce is made by melting together various clayey bodies and soda, the resultant glass being then crushed, hydrated and washed repeatedly. It is then screened, dried in centrifugal machines and stored moist. The finished product is of a grey, mother-of-pearl luster and quite insoluble in water.

The properties of exchange mentioned above are those on which is based the use of Permutit in water softening. Hard waters contain salts of lime and magnesia—chiefly bicarbonates, sulphates or chlorides. To these salts are due all the soap destroying effects, boiler scale formation, and the many other disagreeable qualities of hard water. Suppose now we allow a hard water to flow through a bed of Sodium Permutit. Just as explained above the lime and magnesia in the water displace the sodium of the Sodium Permutit forming Calcium or Magnesium Permutit, while the sodium goes away in the water as soluble sodium salts.

Calling the acid radicle of the Sodium Permutit P, the softening action of Permutit is expressed by the following equations:

$$Na_2P + CaSO_4 = Na_2SO_4 + Ca.P.$$
$$Na_2P + MgCl_2 = 2NaCl + Mg.P.$$
$$Na_2P + CaH_2(CO_3)_2 = 2NaHCO_3 + Ca.P.$$

In practice, this exchange is absolutely complete. A water charged with a lime salt will come out after filtration absolutely lime-free and magnesia-free, and will contain no scale-forming, soap-destroying or other injurious ingredients. Treated with ammonium oxalate, for example, the treated water remains quite clear, while if tested in the usual way with soap solution the water will be shown to be of zero degrees of hardness. This property of exchange may be shown in striking fashion by taking a water saturated with calcium sulphate. Such a water gives a thick curdy mass with soap solution—for example, the Boutron-Boudet solution—and it is impossible to estimate the hardness accurately. Let the water now pass through Permutit and it will be found that with 40 cc. of treated water 3-5 drops of

Digitized by Google

soap solution produce a lasting lather. The water is a "zero" water.

In course of time obviously the Sodium Permutit with which we began will have all its sodium displaced and will have become a Lime-magnesia Permutit in accordance with the equations given above. Lime-magnesia Permutit has naturally no effect on hard water. Use is now once again made of the "base exchange" property of the Permutits. Through the bed of Lime-magnesia Permutit allow a solution of common salt to flow. Then the sodium of the salt replaces the calcium and magnesium of the Calcium Permutit, forming Sodium Permutit again, while the calcium combines with the chlorine of the salt according to the equation:

$$CaP + 2NaCl = CaCl_2 + Na_2P.$$

It is then only necessary to wash away the excess of salt and the expelled $CaCl_2$ and we are left with a bed of Sodium Permutit ready for work again. In the process of softening then, the following cycle goes on indefinitely:

In *Working.* Sodium Permutit + Hard water (= Calcium salts) = Calcium Permutit + Sodium Salts (soluble).

In *Regeneration.* Calcium Permutit + Sodium Chloride = Calcium Chloride + Sodium Permutit.

The softener consists of a cylindrical tank containing a bed of Sodium Permutit between two layers of gravel. The hard water enters at the top and percolates downwards, the rate of flow being adjusted so that a zero water flows away underneath. A given weight of permutit treats an amount of water varying, of course, directly with the hardness. When the specified amount of crude water has passed through, the inlet is closed and the flow of water is reversed for a minute or so. This reversal of flow breaks up the bed and prevents formation of channels, expels air, etc., which may have collected in the pores. The filter thus cleansed is ready for regeneration. Above the cylindrical tank is another tank into which the necessary amount of salt is introduced and dissolved in water. This solution is run in on to the Permutit, and the outlet cocks are so arranged that the salt solution flows through in about six to eight hours. At the end of this time the salt valves are closed and the filter is washed free from chlorides. It is then ready for work again.

Digitized by Google

The softener may be of the open or closed (pressure) type. By having a lid bolted on, as in the pressure type it can be put anywhere in the water supply circuit. This is an advantage. The whole arrangement is very simple, and there are no moving parts or proportioning gear. Common salt is the only reagent used, and is not of the same objectionable nature as lime or soda. The water coming out is of exactly the same alkalinity as that entering, except that it contains no lime. It requires just as much acid to acidify it before treatment as after treatment. This is an important point. The treated water is of the same reaction entirely. The lime goes away in washing as soluble chloride of calcium, so there is no sludge to dispose of and no settling tanks or filters are necessary. In every other softener precipitation methods are resorted to—calcium salts having to be precipitated by lime or soda added in specified quantities—producing disagreeable precipitates of calcium carbonate, etc., which have to be mechanically removed. In such machines large clumsy settling tanks are necessary, and a fine adjustment of the quantity of chemicals added is indispensable.

Permutit water has the advantage of being of uniform quality. It is zero all the time. Suppose a plant is designed to treat a maximum of say 10,000 gallons. Then enough Permutit is put into the filter bed to remove the lime from 10,000 gallons, so that from start to finish an absolutely lime-free water is produced. Such a uniformity is of great advantage in every factory, and there is no continual adjustment of chemicals necessary to obtain this end. In the case of a lime-soda plant the hardness rarely falls below three-fourths degrees unless an excess of reagent is added, which is in itself a serious objection.

In this paper I shall deal with only one other member of the Permutit series—namely, the product known as Manganese-Permutit. It is possible to replace the sodium in Permutit by manganese and so form a Manganese-Permutit. This is a silicate of exactly the same porous and amorphous nature as the other Permutits. If now we act on this substance with a dilute solution of potassium permanganate, the manganese element in the Permutit is oxidized to the higher oxides of manganese and Potassium Permutit is formed. These oxides of manganese are

Digitized by Google

precipitated in an extremely fine state of division in and on the Permutit, and the whole mass becomes black or brown. This mass is very rich in oxygen and is a very powerful oxidizing agent, being composed of mixtures of several of the higher oxides. If now this manganese Permutit, as it is called, be allowed to act upon easily oxidizable matter, the latter is immediately oxidized at the expense of some of the oxygen in the Permutit. In time, naturally, all the oxygen is used up; it is then only necessary to recharge the mass with oxygen by allowing a solution of potassium permanganate to flow slowly through it. This regenerates the Permutit, yielding up its oxygen to it and making it highly active again. This is the analogous process to the regeneration by salt, in the case of Sodium-Permutit in water softening.

This property which Manganese Permutit has, of assimilating oxygen and yielding it up again readily, has been turned to account on an industrial scale for the removal of iron from waters, for the removal of manganese in any form from waters, and for the sterilization of water.

Suppose we have a filter filled with Manganese-Permutit, and we filter water containing iron through it. The iron is oxidized by the high oxides of manganese which are precipitated in the Permutit. Oxide of iron is thereby precipitated in the upper layers of the filter bed, and a water chemically free from iron passes through. There are no traces left, and the water is not only, as we say, commercially free from iron but absolutely so. In time, of course, if we pour more iron solution through, we should use up all the oxygen from the active oxidation material, and we would then have to regenerate. In practice the filters are all built of a pressure type with stirrers inside to prevent choking up by the precipitate of iron. In form the filters are practically the same as the softeners, there being the usual regeneration tank, this time for $KMno_4$. When regeneration is necessary we have first to close the inlet cocks and wash from the bottom upwards for some time, thus washing away the accumulated mud of iron oxide. When the outflow is clear we begin regenerating, allowing the $KMnO_4$ solution to flow slowly through the bed. At first the outflowing liquid will be quite

Digitized by Google

clear and colorless. This indicates that the potassium permanganate is being acted upon and discolored in the filter bed. In point of fact, the exhausted Permutit is acting on it, precipitating all the manganese out of it as higher oxide of manganese, and a manganese-free water is flowing through. This process of regeneration can be readily demonstrated. If we take a filter which has been used somewhat and pour permanganate through, the liquid will come out clear and free from manganese. The more oxides of manganese we get in the filter, the better it is, for they easily oxidize on regeneration and yield thereby a larger amount of available oxygen. In one particular filter, the activity had risen ten-fold after ten regenerations. Some waters containing much organic matter and much iron combined with organic acids are particularly hard to treat. To such as these it is customary to add dilute potash permanganate solution in the form of drops to the crude water. This is easily done, the $KMnO_4$ being sucked in by the flow of crude water in the inlet piping. This permanganate acts upon organic matter, colloidal oxides of manganese are formed, and aid in the deposition of the iron. The last traces of the excess of manganese or permanganate are, of course, subsequently removed by the Permutit.

Sterilization of water by Manganese-Permutit is also carried out in this way. Very many waters do not become sufficiently sterilized by simple filtration, especially where there is much organic matter present which uses up the oxidizing agents and oxygen in the water. In sterilization by Permutit, permanganates are added to the water; these help in the killing of the germs and produce in presence of manganese salts colloidal hydroxides, which precipitate and coagulate all harmful organic matter. Any excess of permanganate is removed on filtering through Manganese-Permutit.

The main interest, however, which Manganese-Permutit has in the industrial world is on account of the facility with which it removes iron. As already stated, we get a water after filtration absolutely free from iron. There can be no danger to manufacturers from iron stains which have a way, when traces of iron are present, of developing long after finishing the goods.

Digitized by Google

THE ESTIMATION OF POTASSIUM, ESPECIALLY IN FERTILIZERS, SOIL EXTRACTS AND PLANT ASHES.[1]

By William A. Davis, B.Sc., A.C.G.I.

It is still no uncommon occurrence to find the results returned for potassium by different analysts, even by those with special experience in this field, differing by very large amounts, in cases where there can be no possibility that the difference is due to sampling. In one case recently that came within the writer's experience, the results returned by two well-known London analysts differed by as much as 3 per cent. on a sample of 90 per cent. sulphate of potash. The writer, therefore, has subjected the present methods of analysis to an experimental investigation. The details will be published elsewhere, but the main results can here be briefly stated.

Considerable differences exist in practice as to the concentration of the alcohol used in taking up the syrupy mixture of sodium and potassium platini-chlorides in order to separate the former, which is the more soluble. Many chemists adopt 80 per cent. alcohol, as rceommended by Fresenius (*Zeit. Anal. Chem.*, 1877, 16, 63), but others follow Precht (*Zeit. Anal. Chem.*, 1879, 509) in considering that absolute or high-percentage alcohol is preferable. This is the practice of the Stassfurt chemists, and Tietjens, in his article on Potash Salts in Lunge's *Chem. Tech. Untersuchungsmethoden*, bases this view largely on the fact that potassium platini-chloride is less soluble in absolute alcohol (1 in 40,000) than in 80 per cent. alcohol. He considers the fact that more correct results are obtained by many chemists using 80 per cent. alcohol to be due to a "compensation of errors." In an important paper in 1906, Morozewicz (*Bull. Acad. Cracovie*, 1906, 796) contended that if absolute alcohol is used, not only are high results usually obtained, especially when sodium salts are present, but that three or four times more platinum chloride is necessary to keep the whole of the sodium in the form of Na_2PtCl_6 than when 80 per cent. alcohol is used.

The writer has fully confirmed Morozewicz' statements. Using a mixture of 0.1 gram KCl+0.1 gram NaCl and more than

[1] *Chemical World*, July, 1912, I, pp. 219-20.

Digitized by Google

sufficient platinum chloride to convert both the chlorides to platini-chlorides, very high results were obtained (*e.g.*, 122.5 per cent. and 119.3 per cent. of the actual) for the K_2O present, when 95 per cent. alcohol was used for extraction and washing (105—110 cc. of alcohol being used in all). On washing *once* with 50 cc. of 80 per cent. alcohol on the other hand, the results became correct (99.4-100.4 per cent.); it was found that sodium chloride was dissolved by 80 per cent. alcohol out of the precipitate obtained with 95 per cent. alcohol, and could be recovered from it. But the platinum method, even using 80 per cent. alcohol, is always subject to the error that every successive 50 cc. of alcohol used in washing dissolves about 2 milligrams of K_2PtCl_6. In the case of small precipitates, such as are dealt with frequently in the case of soil extracts, this relatively large amount may cause very serious error. There is always, too, the difficulty of recognizing when the precipitate is just sufficiently washed; every additional washing lowers the result considerably.

Such error could of course be eliminated by using 80 per cent. alcohol previously saturated with potassium platini-chloride for the washing.

Another grave source of error is found in analyzing potash materials containing sulphates; in such case the sulphate has to be turned into chloride by treatment with barium chloride. In the Stassfurt method the precipitation has to be carried out very exactly, as a slight excess of either sulphate or barium chloride is very prejudicial. High results are easily obtained unless great care is used.

In Germany, the perchloric acid method has almost superseded the older platinum method (Precht, 7th *Intl. Congress App. Chem.*, 1909, Section I., p. 146), not only on the ground of economy (which at the present time, with platinum at £13 per ounce, is a matter of great consideration), but in view of greater simplicity of working, and as being less liable to error, especially in dealing with sulphates. The writer has tested this method very thoroughly by using pure potassium salts either alone or in presence of other salts. It was found that even with small quantities of potassium very exact results were obtained; and that in such cases there is no necessity to convert the sulphate present into

Digitized by Google

chloride by prior treatment with barium chloride. Thus a mixture of pure potassium chloride and sulphate containing 0.0307 gram K_2O gave with the perchlorate method in successive results (1) 0.0305, (2) 0.0312, (3) 0.0305, (4) 0.0306, (5) 0.0307 gram K_2O. Using 0.10 gram of pure K_2SO_4 (representing 0.0541 K_2O), without any treatment by barium chloride, results (1) 0.0536, (2) 0.0536 gram K_2O were obtained. Using 0.10 gram of pure KCl, mixed with double this quantity of sodium chloride, sodium phosphate or calcium chloride, quite correct results were obtained, the added salts not interfering in the least. The same is true of barium chloride, which can be present in considerable proportion without causing trouble. Only in the case of large amounts of magnesium salts was difficulty encountered, when high results were obtained, unless the magnesium was previously removed.

The perchlorate method has been applied by the writer with advantage to the analysis of soil extracts, plant ashes, and ashes obtained on evaporating the crude liquors of the manufacture of organic acids. The procedure is briefly as follows:—The solution of chlorides, containing iron, aluminum, phosphates, etc., is evaporated to dryness as in Neubauer's method (*Landw. Vers. Stat.*, 1906, *63*, 141) and ignited at a dull red heat. When magnesium salts are present, as is usual, after all hydrochloric acid is removed, 0.5 to 1.0 gram of barium hydroxide is added. After ignition, the residue is extracted with boiling water, filtered into a glass dish, 2.5 to 5 cc. of 20 per cent. perchloric acid solution (sp. gr. 1.125) added, and the colorless solution evaporated nearly to dryness, until copious fumes of perchloric acid are evolved. The syrupy mass is then taken up with 20 cc. of 95 per cent. alcohol, and the residual potassium perchlorate transferred either to a Gooch cruicible (with a layer of asbestos at least one-eight inch thick) or to a filter paper which has previously been dried and weighed in a stoppered weighing bottle. It is washed with 30 to 70 cc. of 95 per cent. alcohol, to which 0.2 per cent. perchloric acid has been added, and then with 95 per cent. alcohol alone, until the washings are free from acid, as tested by sensitive litmus paper. The precipitate is dried to constant weight in a steam oven. One milligram $KClO_4$=0.340 milligram K_2O.

Digitized by Google

In view of the grave errors to which the platinum method is subject, there seems no good reason for longer retaining it, in view of the fact that a more accurate and simple method of analysis exists in the perchloric method. Its abandonment is, moreover, desirable not only on grounds of economy, but as eliminating the vexed question as to the value that shall be chosen for the atomic weight of platinum in potash analyses (see Precht, *Intl. Congress App. Chem.*, 1909, Section I). In the perchloric acid method the ratios involved are the simple molecular ratios such as $\frac{KClO}{KCl}$, or $\frac{2KClO_4}{K_2O}$, in which the atomic weights used have all been accurately fixed.

TANNIC ACID, ETHYL GALLATE, AND THE SUPPOSED ESTER OF TANNIC ACID.*

By H. C. Biddle and W. P. Kelley.

The optical activity of tannic acid has led many investigators to seek an adequate explanation of this phenomenon. The original digallic acid formula of Schiff[1] contains no asymmetric carbon atom and consequently fails to explain the behavior of the substance towards polarized light. Schiff[2] suggested the existence of a ketone group in the digallic acid structure, while Walden[3] concluded that the optical activity is due to the presence of some other body or bodies associated with tannic acid and from which separation is very difficult. Rosenheim and Schidrowitz[4] found on the other hand that by certain methods of purification a product may be obtained from tannins of varying optical activity, which has a constant specific rotary power of about + 75.5°. They also noticed that the acetyl derivative as also the quinine salts obtained from tannic acid, showing a wide range of variation in optical activity, were almost identical in specific rotary power, regardless of the source from which they were derived.

* *Jour. Am. Chem. Soc.*, July, 1912, pp. 918-23.

[1] Schiff, *Ber.*, **4**, 231, 967 (1871).

[2] Schiff, *Gazz. chim. ital.*, **25**, 437 (1895).

[3] Walden, *Ber.*, **30**, 3051 (1897).

[4] Rosenheim and Schidrowitz, *J. Chem. Soc.*, **73**, 878 (1898).

Digitized by Google

Nierenstein[5] has devoted considerable study to this question with particular reference to certain derivatives of tannic acid and concludes from his investigations that tannic acid consists of equal parts of digallic acid and a substance called by him leucotannin which is supposed to contain an asymmetric carbon atom.

In the various investigations dealing with tannic acid from the middle of the last century down to the present time, it has been repeatedly noted that the acid contains glucose. Strecker,[6] for example, pointed out as early as 1852 that upon hydrolysis tannic acid yields gallic acid and glucose. Since that time similar observations have been made repeatedly. Of particular interest here from the synthetic standpoint is the recent preparation by Fischer[7] of Penta-galloyl-glucose and similar substances.

In the preparation of so-called pure tannic acid the separation of impurities is extremely difficult from the nature of the substance. In fact it may well be doubted whether chemically pure tannic acid from natural sources has ever been obtained. The purification of colloids presents almost insurmountable difficulties. It seems, therefore, not at all impossible that the optical properties of tannic acid may after all be due to the presence of glucose whether occurring as an impurity or in some essential combination of the nature of a glucoside.

As is well known the natural tannins are capable of fermentation.[8] One of the commercial methods for producing gallic acid, indeed, depends on this fact.[9] It, therefore, is of some interest to study the effect of fermentation under varying conditions on the optical properties of pure tannic acid. If the optical properties are due to the presence of glucose either as an impurity or as an essential part of the tannin, it is conceivable that fermentation of the glucose into carbon dioxide and alcohol might, under some conditions, lead to an extinction of the optical activity without completely hydrolyzing the tannic acid to gallic acid.

Action of Microörganisms.—The fact that various fungi will develop on solutions of tannic acid is a matter of common obser-

[5] Nierenstein, *Ber.*, **41**, 77, 3015 (1908); **43**, 628 (1910).
[6] Strecker, *Ann.*, **81**, 248 (1852).
[7] Fischer and Freudenberg, *Ber.*, **45**, 915 (1912).
[8] Tieghem, *Z. Chem.*, **1868**, 222.
[9] Allen's, "Com. Org. Analysis," 4th edition, Vol. 3, p. 526.

Digitized by Google

vation among pathologists. Pottevin and Fernback[10] claim that the fungus, *Aspergillus niger,* when grown in solutions containing tannic acid develops an enzyme, tannase, which can be extracted from it by means of alcohol and which has the property of splitting tannic acid into free gallic acid and glucose. Some preliminary study of the action of this fungus has been made. We have found that pure cultures of the fungus can be easily grown in sterile solutions of tannic acid, and that the solutions subsequent to the development of the mycelium still give the reactions of tannic acid, but do not contain large quantities of gallic acid.

A few preliminary experiments have been made regarding the action of yeast (*Saccharomyces cerevisiae*) upon tannic acid. Samples of the purest tannic acid obtainable, including a sample of Baker's highest purity and one from the German firm of Schering, were dissolved in water to a 4 per cent. solution, sterilized and then inoculated with pure cultures of yeast. After an incubation period of ten days, it was found that in every instance alcoholic fermentations had taken place. Portions of the solutions were distilled off and the distillate tested for alcohol by means of the iodoform reaction. The presence of alcohol was shown in every case. The specific rotatory powers of the several samples before fermentation varied from $+10°$ to $+55°$, but in every instance the action of the yeast cells totally destroyed the optical activity. Portions of the fermented solutions after being freed from aggregates of yeast cells were found to give the characteristic reactions of tannic acid, such, for example, as the precipitation of solutions of gelatin and ammoniacal solutions of copper sulfate. The content of gallic acid appeared to have increased to some extent as shown by the reaction with potassium cyanide, although the conversion to this acid was far from complete.[11]

The preparation and isolation of a definite crystallin compound of tannin containing glucose as a necessary constituent of the

[10] Pottevin and Fernback, *Compt. rend.*, 131, 1214 (1900).

[11] The conversion of tannin into gallic acid by atmospheric fermentation, as it is practiced in the commercial production of gallic acid, probably results from the combined action of various microörganisms, rather than from that of a single species.

Digitized by Google

molecule would bring strong evidence to support the glucoside charcter of natural tannin. In 1910 Manning[12] published an article in which he claims to have synthesized such a compound, ethyl tannate (m. p. 157°), and gives evidence showing apparently that glucose forms an integral part of the molecule. The importance of such an observation, if correct, in throwing light on the constitution of tannin itself is self evident. As the method of synthesizing the so-called ethyl tannate seemed a litle extraordinary in view of the ready hydrolysis of tannin to gallic acid, we took occasion to repeat Manning's work. The results, however, were entirely different from those of Manning. The ester obtained was found to be invariably ethyl gallate, differing in no way from the ester synthesized from pure gallic acid. Further study of his work revealed the fact that his method for estimating glucose in the supposed ethyl tannate is unreliable. Moreover the peculiar properties of pure ethyl gallate when melting, as developed in our study, lead to the conclusion that Manning has simply mistaken this substance for ethyl tannate.

The Work of Manning.—In repeating Manning's synthesis the tannin used was that from Schering. This was purified and treated in exact accordance with the directions of Manning. The ester obtained from extraction with chloroform, we found as he states, forms pale yellow, spherical nodules, but an examination of the substance showed it to be identical, as we have indicated, with ethyl gallate prepared by similar methods from pure gallic acid. Thus, mixtures of the crystals of ethyl gallate and the supposed ethyl tannate obtained by crystallizing the two from ether-ligroin showed no variation in melting point or in any other property from ethyl gallate itself. An analysis of the supposed ethyl tannate recrystallized from ether-ligroin gave the following results:

0.2 gram substance gave 0.3990 gram CO_2 and 0.0946 gram H_2O.

Calculated for ethyl gallate:	C, 54.54; H, 5.05.
Found:	C, 54.4 ; H, 5.2.

In Manning's work determination of glucose in tannin as well as in the supposed ethyl tannate was made by hydrolyzing these substances with hydrochloric acid and extracting with either six

[12] Manning, *J. Am. Chem. Soc.*, **32**, 1312 (1910), this J., V, 513.

Digitized by Google

times to remove gallic acid. The solution which was thus supposed to have been freed from all but traces of gallic acid was then used as a basis for the estimation of glucose, a certain correction being made for the glucose which had been dissolved in the ether during extraction.

In this method the mistake is made of assuming that six extractions with ether under the conditions given are sufficient to remove from the solution all but traces of gallic acid. If, for example, pure ethyl gallate is submitted to Manning's method of procedure, the solution remaining after extraction with ether gives vigorous reaction for gallic acid with potassium cyanide, providing excess of hydrochloric acid is *first* neutralized with sodium carbonate, and, furthermore, it contains ordinarily sufficient gallic acid to account for all the reducing action which Manning attributes to the presence of glucose. These results are not materially affected whether the ether used in extraction is the ordinary washed ether or that of the highest purity. Thus, an application of Manning's method to 0.2 gram of pure ethyl gallate synthesized from Kahlbaum's pure gallic acid led to a reduction of Fehling's solution which estimated as glucose amounted in one case to 16.4 per cent. and in another to 15.8 per cent. (Manning[13] estimates glucose in his supposed ethyl tannate to be 15.38 per cent.)—and this in a substance absolutely devoid of glucose!

It follows from these considerations that the results of Manning's investigation must be regarded as unreliable and the supposed ethyl tannate becomes in all probability identical with ethyl gallate. The source of the confusion of ethyl gallate with a supposititious ethyl tannate lies in the failure of Manning to note the peculiar behavior of ethyl gallate on melting—a peculiarity apparently hitherto entirely unnoted by other investigators as well, in the case of this particular ester.

Ethyl Gallate.—In the literature three melting points are recorded for ethyl gallate. Grimaux[14] finds a melting point of 158 degrees; Ernst and Zwenger[15] record a melting point of 150 de-

[13] *J. Am. Chem. Soc.*, **32**, 1317 (1910).
[14] Grimaux, *Bl.*, **2**, 94 (1864).
[15] Ernst and Zwenger, *Ann.*, **149**, 29 (1871).

Digitized by Google

grees; and Etti[16] states that the ester melts at 141 degrees. The result of the last determination is assumed by Manning[17] to be correct and since he finds for his substance synthesized from tannic acid a melting point of 157 degrees he reaches the conclusion that it is not ethyl gallate but ethyl tannate.

A study of ordinary ethyl gallate reveals peculiarities in its melting point which at first glance strongly suggests the possible phenomenon of liquid crystals, or the existence of two crystallin phases. As prepared from pure gallic acid and purified by crystallization from chloroform or by careful sublimation, the ester forms a mass of long, fine, white, silky needles. These when melted ordinarily begin to sinter down near 145 degrees and melt to a turbid liquid at 149-150 degrees, which only becomes clear at 157-158 degrees. The supposed ethyl tannate of Manning behaves in precisely the same way. The possible contamination of ethyl gallate with an impurity led us to a comparison of our product, which had been synthesized from Kahlbaum's pure gallic acid, with products obtained from other sources. The same phenomena were observed in all specimens. We then submitted ethyl gallate to careful purification by recrystallizing it successively from chloroform, ether-legroin and water. The hydrated ester was then freed from water of crystallization and carefully sublimed. A product was thus obtained which sinters down at about 148-149 degrees and melts as before at 149-150 degrees to a turbid liquid which clears at 157-158 degrees. Through a range of fully 8 degrees the liquid remains distinctly turbid, becoming somewhat less dense as it approaches 157-158 degrees, but clearing fairly sharply at this temperature. On remelting the solidified ester, the same phenomena are repeated. If, however, the temperature is raised about 8 degrees above 158 degrees before the fused mass is cooled, the solidified ester now melts to a *clear* liquid at 149-150 degrees. If, on the other hand, during the process of cooling from the higher temperature, the clear fused mass is inoculated with a trace of the unfused substance near 150 degrees, the turbid state is apparently slowly reinduced before solidification takes place.

[16] Etti, *Ber.*, **11**, 1882 (1878).

[17] Manning, *J. Am. Chem. Soc.*, **32**, 1316 (1910). This J., V. 573.

Digitized by Google

The appearance of ethyl gallate between crossed nicols during the process of fusion strongly suggests a case of crystallin polymorphism not unlike that observed by Pope[18] in the case of chloral and somewhat similar to that noted by Offret and Vittenet[19] in the case of di-*m*-nitro-*s*-diphenylcarbamide. A suitable hot stage for the study of the phenomena of fusion was found in a thinly platinized glass slide whose resistance to the passage of the electric current afforded ready production and control of the temperature desired.[20] In order to obtain the ethyl gallate in a form suitable for examination, a little is fused down on the microscope slide either with or without the addition of a cover glass, and the whole is allowed to cool. A casual inspection of the film under the polarizing microscope between crossed nicols shows ordinarily what appears to be a mixture of crystallin plates and hair like needles or sheaf like groups of needles. If the temperature is now gradually raised, very slight alterations are observed in the preliminary softening. These are followed by a melting process in which the plate-like crystals fuse to a clear liquid, leaving the more or less intricate mass of hair-like needles unchanged. As the temperature continues to rise these in turn disappear and the liquid becomes clear. On recrystallization during cooling, ordinarily both forms of crystals are reproduced, the needles and the plates. If, however, the fusion is carried to the point of removing from the slide every trace of needles, on cooling but one form of crystals, the plates, are produced and these on fusion now melt to a *clear* liquid without showing any presence of needles. But if the crystallin plates are allowed to stand at the ordinary temperature for about twelve hours, they are largely converted into the hair like needles as may be shown by a repetition of the phenomena of fusion noted in the first instance.

It would seem, then, that ethyl gallate probably presents two crystallin phases, one the hair like needles, stable at ordinary temperatures, the other, the flat plates stable, if stable at all, at

[18] Pope, *J. Chem. Soc.*, **75**, 455, (1899).

[19] Offret and Vittenet, *Bull. soc. fr. min.*, **22**, 69 (1899); *Z. Kryst.*, **34**, 627 (1901); *J. Chem. Soc.*, **76**, 886.

[20] We are indebted to Dr. F. G. Cottrell, formerly of this University, and now of the U. S. Bureau of Mines, for the apparatus here used, a description of which will appear soon.

Digitized by Google

more elevated temperatures, and that further the turbid condition of the fused ester is apparently due to the presence of masses of unfused needles.

These suggestions are advanced tentatively as the phenomena in question have as yet been only incompletely studied. The investigation, however, is being continued particularly to determine with certainty whether or not the case is actually one of crystallin dimorphism and, if so, to learn the habits of the two crystallin forms and the exact conditions under which one crystallin phase passes into the other.

The peculiar behavior of ethyl gallate on fusion, however interpreted,[21] serves not only to explain the divergence in melting points given for this substance in the literature, but also probably explains, in part at least, the mistake of Manning[22] who, assuming that ethyl gallate melted at 141 degrees, concluded that the substance melting or changing at 157 degrees must be another substance.

HENRY RICHARDSON PROCTER.[1]

Among those who have helped to transform leather manufacture from an "art and mystery" to a scientific process, no one man has been more widely known and honored than Professor Procter. In our last issue mention was made of the fact that he had been presented with the freedom of the Leather Sellers' Company. The actual investiture took place at a meeting of the Company on June 12, on which occasion Mr. John Pullman, Worshipful Master of the Company of Leathersellers, gave an outline of Procter's life and work and then formally presented

[21] It is to be noted that the ethyl gallate prepared by Etti and melting at 141° was obtained from gallic acid derived from the so-called *kinvin*. A further study of gallic acid from this source to determine whether or not it is really identical with ordinary gallic acid seems desirable.

[22] In a letter just received from Prof. W. Lash Miller (under whom Mr. Manning carried out his work) in response to a request for a specimen of the so-called ethyl tannate, Prof. Miller likewise states that he has repeated Manning's work and has been able to get only ethyl gallate, instead of ethyl tannate.

[1] For the facts of this sketch we are indebted to the *Leather World*, of June 13, 1912.

Digitized by Google

to him the "freedom" of the company, and invested him with its livery. It would require much careful study of the Medieval trade guilds of England and their rites and ceremonies to give an American any real comprehension of the meaning of the terms and ceremonies involved, but it requires no study nor imagination on the part of any leather chemist in the world to understand that this ceremony, whatever its mystic content, expressed on the part of the British leather trade high appreciation of the magnificent services rendered to their guild by Henry R. Procter.

Nothing mentioned in Mr. Pullman's sketch is more striking than the fact that Professor Procter has reaped no pecuniary reward from his many important discoveries. He has been a teacher in the leather industries department of Leeds University for many years, and has followed the best traditions of his profession in dedicating the results of his researches to the benefit of mankind. His countryman Michael Faraday and our own Joseph Henry and Samuel P. Langley are examples in different fields of scientific research of the same unconscious and uncalculating self-sacrifice.

Born in 1848, Henry R. Procter is the son of John R. Procter, a tanner of North Shields. Being of Quaker ancestry, he was educated at Friend's School at Boothan, York, a notable institution from which have come such men as John Bright, Silvanus P. Thompson, and Dr. Spence Watson. Later he studied at the Royal College of Chemistry and School of Mines. He was connected with the tanning business of his father until the death of the latter in 1888. After that for three years he was chemist for E. and J. Richardson, Newcastle on Tyne, and then he was selected to take charge of the newly established Leather Industries Department at Leeds University. From this position he will retire next year on account of the age limit.

The Text-book of Tanning was published in 1885, Principles of Leather Manufacture in 1903, and Leather Industries Laboratory Book in 1898 and republished in 1908. Procter has also written very many articles on leather topics. He was one of the originators of the International Association of Leather Trades Chemists and has always been a leading spirit in it. Leather chemists every where unite in the hope that in spite of his re-

Digitized by Google

tirement from the teaching force at the University, Henry R. Procter may long continue to contribute to the literature of their branch of science.

BOOK NOTICES.

TANNERS' YEAR BOOK, 1912. Organ of the United Tanners' Federation of Great Britain and Ireland. Compiled by Charles E. & J. Gordon Parker. For sale by W. B. Moston, Penketh, near Warrington; 2s. 9d. post free.

Some fifty of the 161 pages are taken up with statistics, etc. Signed articles are as follows: Franco-British Leather Trade, Robert Walton; The United States Leather Company, C. E. Parker; Tanners' Problems, George Randall; Classification and Weighing of Hides, Owen Turner; The "Allied Trades Committee," Alfred Seymour-Jones; Waste, Ernest D. Evans; Exports of Boots and Shoes, C. E. Parker; Goosypium Herbaceum, Charles Prescott; The Classification, Weighing and Flaying of Hides, Robert Harrison; Advantages of the Graphic Method of Recording Tannery Results, by C. E. Parker; The Bristol Port Authority, William Howell Davies; Roller Cloth for Cotton Spinning, Herbert Fletcher; The Soaking of Dried Hides by means of Formic Acid, J. R. Blockley; Extracts, Highly Concentrated and Dry Extracts, William Aitken; Smyrna and Its Trade with Great Britain, Richard Whittall; Rising or Pickling of Skins, J. T. Wood; Chemistry of Tanning, Extracts of Year's Work, Stanley Hirst; The Designing and Equipment of Leather Manufactories, M. C. Lamb; History of the Valonia Trade, J. G. Parker; the Labor Unrest, W. Dove Willcox; The Weighting of Present-day Leather, A. Lovell. Two of these articles are reprinted in this issue of the JOURNAL. Abstracts of several others will appear later.

HIDES AND SKINS. Compiled and published by A. H. Lockwood, of the *Shoe and Leather Weekly*, Chicago. 247 pages, 5 x 7½ inches. Illustrated. $5.

It is stated on the title-page that this book is "written by specialists and authorities in the several departments of the Hide and Skin Industry." Although a number of the articles are signed, much of the space is occupied by unsigned matter. This

Digitized by Google

we infer is from the pen of Mr. Lockwood who is certainly an authority on most departments of the industry. The first chapter (10 pages) on hide fiber is by Robert W. Griffith. It tells the little that is known about the chemical constitution of hide, describes the arrangement of parts in the hide, tells about preservative processes, about salt stains, etc., and about the effect of tanning on the fiber.

The second chapter (63 pages) is on domestic hides and skins. It is unsigned, and we therefore credit it to Mr. Lockwood. It describes in detail the processes of slaughtering, flaying, salting, etc., also the principles on which hides are sorted and the various kinds of damage to which they are liable. Market conditions are discussed at some length. There are sections on calf-skins, horse-hides, pig-skins and sheep-skins.

The next chapter on anthrax (18 pages), is by Henry J. Washburn, of the Bureau of Animal Industry. The Method of immunizing cattle by inoculation with attenuated cultures of the anthrax bacillus is described, and results described. Seven pages are devoted to laws and regulations in regard to disinfection of hides.

The next chapter (22 pages) is on progress and prospects of tick eradication, by Dr. Cooper Curtice. "The hide and skin trade in Great Britain" (14 pages) is unsigned, as are "European hides and skins" (14 pages) and "South American hides' (10 pages). The next is by Walter Haynes, on the hides and skins of Australia (3 pages). There are two pages about Danish calf-skins by V. H. Houlberg, two about New Zealand sheep and lamb pelts (unsigned), and three on Russian pony skins by V. H. Houlberg.

Six full-page half-tones of scenes at the Nijni-Novgorod fair come next, and then a 32-page unsigned chapter on goat-skins. The next chapter is a reprint of Mr. Lockwoods paper from the January (1912) JOURNAL. Mr. Oberfell's paper on sampling leather is reprinted from the January JOURNAL, and Mr. Yocum's on hides from the March number.

The book abounds in valuable information, contributed by those who know, and to any one who has to do with hides and skins in any stage, it is well worth the price.

Digitized by Google

ABSTRACTS.

Chrome Tanning Costs. ALAN A. CLAFLIN. *S. & L. Rep.*, June 20, 1912. The first experiments in chrome tannage, by Knapp, used basic chromium chloride, the "one bath" process. The leather produced had no practical value because it was not fat-liquored. Procter showed that other basic chromium salts could also be used. In this country the best source of chrome is sodium bichromate. This salt contains about 50 per cent. chromium oxide (Cr_2O_3), which at present prices makes the cost per pound of Cr_2O_3 in the form of sodium bichromate almost exactly 10 cents If the potassium salt is used the cost is about 14 cents. Another source is chrome alum, which contains 15 per cent. Cr_2O_3; the cost per pound Cr_2O_3 in this case being from 28 to 30 cents. The chrome is in the right condition for use in the alum, while in the other cases it must be reduced. Ready prepared chrome tanning solutions are sold at a price per unit chrome less than that of chrome alum, but not less than the cost of sodium bichromate plus the cost of reduction. It is wise, however, for the tanner who is not thoroughly equipped with apparatus and chemical knowledge for conducting the reduction to buy the ready prepared solutions, as the difference in cost is a very small item in the cost of the finished leather, and mistakes in the making up of the liquor are liable to cause serious damage. It is not certainly known what the actual tanning agent is, but it seems probable that it is a basic salt of chrome, and not the chromium oxide itself. Some acid also is necessary to carry the chrome evenly into the leather. If a very easily decomposed salt of chromium, such as the bisulphite, is used, there seems to be a tendency to tan only the surface and make a very flat leather. This is the case also when the salt used is too basic. The formula of sodium bichromate is $Na_2Cr_2O_7 + 2H_2O$. In order to release all the chromic acid, an equivalent amount of sulphuric acid is required. The molecular weight of the bichromate being 298, 298 pounds of it take 98 pounds of actual sulphuric acid, or about 105 pounds of commercial acid, which is apt to run 93 per cent. To reduce the chromic acid thus formed about 65 pounds of glucose are required, theoretically. In practice larger quantities are necessary, one reason being loss of volatile intermediate oxidation products. The actual quantity of glucose for 300 pounds bichromate is about 125 pounds. (This estimate is much too high.—ED.) The total cost of reducing 300 pounds of bichromate, putting glucose at 2.5 cents per pound and sulphuric acid at 1 cent, for 325 pounds, is thus about $6.30. This makes about 4⅓ cents per pound of chrome. Sodium bisulphite may be used as a reducing agent instead of glucose. In this case, to reduce 300 pounds of bichromate, 210 pounds sulphuric acid and 930 pounds 35 per cent. bisulphite are required, costing $8.85, or 5.9 cents a pound. To compensate for the increased cost, this process gives more certain results, and it also furnishes to the liquor a quantity of sulphate of soda, which makes less salt necessary. On the large scale, the proper

Digitized by Google

method is to use sulphur dioxide instead of bisulphite of soda. The sulphur is burned, and the gaseous sulphur dioxide passed into the bichromate solution. Low grade molasses may be used instead of glucose.

A New Oxygen Absorption Method for Oils. L. P. WILSON and G. S. HEAVEN. *J. S. C. I.*, June 29, **1912.** About 2 gr. oil is mixed with 1 to 3 gr. kieselguhr and put into a 250 cc. flask, the neck of which is then drawn out and sealed. After heating for an hour at 100° C., and cooling to the temperature at which it was sealed, the tip is broken under water. The weight of water which enters gives the volume of absorbed oxygen, from which its weight may be found. L. B.

Exact Method of Taking Samples for Analysis in Tanning. J. PAESSLER. *Le Cuir*, Vol. 5, Nos. 3, 4, 5, 6, 8 and 9, **1912.** The analysis of vegetable tanning material cannot be so exact as that of mineral matter, but is nevertheless very important. The objection generally raised against such analyses is that different chemists often obtain differing results for the same samples. This, it is said, proves that analysis is useless, whereas the fact of the matter is that the method of taking samples is at fault. If a chemist draws attention to this he is invariably informed that no instruction is needed in taking samples, but experience shows otherwise. A load of bark may be from very different trees, and the composition of various pieces may be very different. Therefore a random sample does not represent the whole lot. In taking a sample one should try to get small pieces of as many kinds of bark or other material as possible, so that the result of analysis may be an average. Even if the tanning material is powdered, it cannot be taken for granted that it is homogeneous, because experience has shown in oak, mimosa and willow, for example, that the finely powdered part has a higher tannin content than the fibrous part. This necessitates, as the first requirement of accurate sampling, a thorough mixing of the material to be analyzed, and the taking of samples from many bags.

With nuts—such as myrobalans and valonia—special difficulties arise because not only do individual specimens differ much among each other, but the different parts have varied tannin contents and the nuts are apt to fall to pieces in transportation. Thus these parts settle away from each other, so especial care must be taken in mixing. Solid quebracho extracts in blocks and liquid extracts cannot be considered as homogeneous, but various blocks and barrels must be sampled and these mixed to make the sample to be analyzed.

In taking samples of fats used in tanning care must be exercised, but these materials are much more likely to be uniform in character than are tanning materials.

In sampling leather it is best to take small pieces from all parts and from several hides in a lot.

Having thus reviewed the matters to be kept in mind in sampling all sorts of materials, the actual methods recommended are as follows:

Digitized by Google

(1) *Bark in Bundles.*—Small pieces should be cut from at least 3 per cent. of the bundles, and these pieces put together to form the sample, which should weigh at least one kilo.

(2) *Ground or Powdered Tanning Materials; also Nuts, etc.*—At least 5 per cent. of the bags should be emptied onto a clean floor and the contents thoroughly mixed. Then several samples should be taken, vertically, from top to bottom of the pile and these mixed. This sample should then be ground and from it the final sample, weighing not less than 500 gr., taken.

(3) *Liquid Extract.*—Take at least 5 per cent. of the casks, of members equally far apart, carefully remove the heads and stir the contents all the way down to the bottom. The stirrer should be a wooden disk pierced with several holes and perpendicularly attached at the middle to a long pipe. This is moved up and down in the barrel. Then at least two spoonfuls should be taken from each barrel and the final sample (150-200 gr.) taken from the mixture should be sealed up in a clean bottle and labelled.

(4) *Pasty Extracts.*—At least 5 per cent. of the packages should be sampled in seven places each, these samples put together and a final one of 150-200 gr. taken and boxed. The instrument for sampling is a copper cylinder sharpened at one end, and has a strong handle at the other. The length of the cylinder should be as great as the thickness of the block. A plug is also used to push out the sample when taken.

(5) *Solid Extracts.*—At least 5 per cent. of the cases should be sampled in various places, these pieces mixed and shipped in air-tight boxes. H. R. Procter recommends that a few drops of turpentine be sprinkled in each box to prevent fermentation.

(6) *Tallow, Wool-grease, Vaseline and Other Semi-solid Fats.*—Take a small sample from several barrels and mix. The final sample should weigh at least 250 gr.

(7) *Fish Oil and Other Liquid Oils.*—Using the same sort of stirrer as for liquid extracts, samples should be taken from 10 per cent. of the barrels.

(8) *Tanning Liquors.*—After stirring the contents of the vat a clean bottle holding at least ¾ liter should be filled and hermetically sealed.

(9) *Leather.*—Take 5 per cent. of the skins choosing those of all sorts and take three pieces from each one; one at the neck, one on the side and one near the tail. Each piece should be labelled.

In general, in taking samples one should strive to get an average sample. Chemists have a right to insist on this and on scientific methods and authorized supervision of the process of sampling.

Comparative Valuation of the Ordinary Deliming Agents. Jos. Hildebrand. *Gerber*, 1912 [38], 129-32, 143-5. The solvent action upon hide substance is also included in the author's research. The agents examined were: (a) sublimed salammoniac 97 per cent.; (b) ammon. butyrate

Digitized by Google

sol. 63.24 per cent., sp. gr. 1.068; (c) butyric acid 82.08 per cent., sp. gr. 0.998; (d) lactic acid 67.84 per cent. free, 11.89 anhydr., sp. gr. 1.218; (e) formic acid 92.5 per cent., sp. gr. 1.213; (f) hydrochloric acid 35.17 per cent., sp. gr. 1.177. For the tests, samples were taken from the head and back of steer hides. These were limed with a paste of slaked lime and calcin, finally dehaired and washed in cold water. Test pieces were cut 8 x 20 cm. and watered for 18 hours before the deliming tests. Smaller samples were meanwhile analyzed with the following results:

	Head	Back
Water	75.15	75.72
Fat	0.254	0.199
Ash	0.448	0.441
Lime: wet hide	0.262	0.255
dry hide	1.068	1.056

Another set of analyses made after 18 hours further watering showed no change in the lime content.

The deliming experiments were made with 1½ liter distilled water containing 1 cc. phenolphthal. sol. (1 per cent.): the first two agents were added directly in slight excess, the acids were added from time to time by a burette to permanent discharge, the first day once an hour, the second day every 2 hours, the third day once in 4-5 hours when the neutralization was practically complete. The delimed hide samples were then hung for 18 hours in a large amount of water in order to remove the lime salts. Samples were then analyzed as follows:

	Head			Back		
		Lime in			Lime in	
	Water	Wet subst.	Dry subst.	Water	Wet subst.	Dry subst.
Salammoniac	73.80	0.157	0.600	68.64	0.198	0.632
Ammon. butyrate	73.39	0.176	0.663	66.74	0.213	0.641
Butyric acid	75.78	0.179	0.739	68.31	0.305	0.961
Lactic acid	76.44	0.160	0.681	68.17	0.265	0.833
Formic acid	75.99	0.164	0.684	66.85	0.296	0.891
HCl	75.07	0.190	0.763	67.62	0.262	0.809

It is remarkable that notwithstanding the complete neutralization and leaching of the soluble lime salt formed, that lime was retained by the hide in larger amounts than that removed. The lime retained is in the form of salt and this shows the need of thorough watering of delimed hides such as for sole and vache leather, which receive no further bateing.

The determination of the dissolved hide substance was made by Eitner's nascent chlorine method. To 100 cc. of the residual deliming liquor were added 10 cc. 12 per cent. sod. hypochlorite sol. and 5 cc. conc. HCl. The pptd. hide was collected on tared filters, washed cold, dried at 100° and weighed. The percentage of hide loss thus found was:

Digitized by Google

	Head	Back
Salammoniac	0.24	0.044
Ammon. butyrate	0.25	0.034
Butyric acid	0.74	0.160
Lactic acid	0.86	0.213
Formic acid	0.44	0.154
Hydrochloric acid	0.42	0.127

The loss of hide in deliming is therefore very small, being greatest with the head pieces and with lactic and butyric acids; these last should therefore be added only from time to time in sufficient amounts to maintain neutrality.

The samples were all afterwards tanned yielding leathers of a uniform character. For deliming on the large scale, especially without expert control, ammonia salts are preferable to free acids and the required amount (or excess) may be added directly. The water of the bath can be often used if partially freed from the ammonia by agitation or slight heating. In the experiments it was found that the residual liquor from the ammonia salt was odorless and free from mold while the liquors from the acids showed decomposition. It may therefore be assumed that the ammonia salts have an antiseptic effect. There is also less dissolved hide to nourish the putrefaction. On the large scale, however, with proper supervision, hydrochloric acid is to be preferred, being cheaper and dissolving least hide.

A series of supplementary experiments with a new deliming agent, "glycoformacin," is also reported. The results are much the same as with formic acid, which appears to be the chief ingredient.

W. J. K.

Bleaching of Upper Leather. *Ungar. Leder Ind.* through *Ledertechn. Rundschau*, 1912, 147. As a rule, this is not needed since weak liquors and light colored tanning materials like oak are used and the leather is well washed before currying. Should bleaching be required, the washed leather is placed in a luke warm bath prepared from the best Sicilian sumac and left a day. A slight after bleaching can be effected with dilute sulphuric acid applied as a bath or wiped over the grain; thorough washing is then needed. After treatment with sulphuric acid a weak solution of lead acetate or barium chloride may be applied which forms an insoluble white sulphate in the pores of the leather. The excess of salt must then be thoroughly washed out. Another bleaching agent is hydrogen peroxide which is applied with a rag to the leather which has been previously moistened with water containing a little ammonia. Another method is an alternating treatment with baths of sod. sulphate and lead acetate. Chrome leather is bleached with dilute hydrochloric acid. Very light, nearly white leather may be obtained by giving an after tannage with sumac and then alternately dipping in sulphuric acid and lead acetate. Chamois leather is first thoroughly degreased by potash in the drum,

Digitized by Google

then washed and agitated about 20 minutes with a lukewarm solution of potass. permang. (of such strength as to have a dark violet color). After rinsing in fresh water, a second bath of dilute sulphuric acid is applied until uniform bleaching is effected. The leather is then washed, pressed, again washed with a little soap, dried and smoothed with pumice. W. J. K.

Tests for Vegetable Tanning Materials in Leather and Commercial Extracts. B. KOHNSTEIN (Address). *Allgemeine Gerber Zeitung*, 1912 [14], No. 19, p. 4. The principal published tests are mentioned, especial reference being made to the lime water tests. Parker and Payne distinguish tannins by the colors thus produced but the author points out that these are greatly affected by mixture conditions and that the age of the extract as well as the manner of clarification employed in its manufacture affect the result. He applies the lime pptn. only to used extract liquors from the coniferous hemlock and pine which give green colors with alkalies; gambier gives a purplish red.

A good reagent for quebracho and mimosa is a drop of conc. H_2SO_4 (65° B.) which gives purple changing to violet, finally becoming brown in the air.

The author has found a distinctive reagent in the "alkutin" of Dr. Paul Meyersberg, Vienna; 10 gms. of this are digested with 100 cc. cold water. If this solution be added to a tannin solution of the concentration used in analysis, characteristic ppts. are formed. Conclusions are, however, based upon the colorless filtrate; this is made alkaline and the following colors are produced: With quebracho extract, yellow, pale reddish on shaking; mangrove, a flesh color, on long shaking deep brick red with a tinge of violet, on heating it becomes intensely flesh colored; knoppern, cold, flesh color, on heating wine yellow. Old extracts of hemlock or pine give foliage green, darkening in the air and disappearing on heating. Sumac and myrobalans give sulphur and lemon yellow, changing to orange yellow on heating. W. J. K.

Kohnstein's New Identification of Tannin. LEOPOLD POLLAK. *Allgemeine Gerber Zeitung*, 1912 [14], No. 20, p. 4. In testing this reaction it was found that mangrove could only be relatively identified. The test was carried out exactly as directed by Kohnstein and succeeded best with sulphited extracts, due to salting out, giving clear filtrates. If the filtrate is milky, it may be clarified with kaolin. The reaction in the cold proceeds as described, but the green of pine is not always distinct. Quebracho extracts often give a dark yellow. On boiling the ammoniacal solution, the results did not agree with Kohnstein's due perhaps to the author's use of clear filtrates. A ppt. resulted, not mentioned by Kohnstein, white with quebracho, rose with mangrove, after filtration and washing, the filtrate being yellow. Sulphited extracts gave no ppt.

Mangrove can be recognized in quebracho extracts not excessively sulphited, if not over 10 per cent. myrobalans are present. Five cc. of

Digitized by Google

10 per cent. alkutin solution are shaken with 10 cc. of tannin solution and a little kaolin, then filtered. A little ammonia is added to the filtrate which is then boiled. The ppt. is filtered and washed, being invisible on the paper with pure quebracho but rose with 10 per cent. mangrove. Any admixture of a yellow pptg. tannin such as chestnut or sumac, obscures the test. Further, maletto gives a reddish ppt. W. J. K.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII SEPTEMBER, 1912 No. 9

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y.

CHANGES OF ADDRESS.

Albert L. Burwell, to Lock Box 208, Winsted, Conn.
George L. Adams, to 303 Fifth Ave., New York City.
Otto Wigaart, to 80 Maiden Lane, New York City.
Elting C. Stilwell, to Allamont, New York.
William H. Gates to "Hollies," 12 E. Cotham Road, Bristol, England.

CONFERENCE OF THE INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMISTS.

Dr. J. Gordon Parker, President of the I. A. L. T. C., has written both to the President and Secretary of the A. L. C. A., extending to all the members of our Association a cordial invitation to attend the Conference of the I. A. L. T. C., to be held in London, Sept. 16th to 20th, 1912.

Digitized by Google

METHODS FOR OIL ANALYSIS.

By Charles Eachus.

Oil analysis is to some extent a matter of guess work, but some chemists can guess better than others. A practical chemist, who familiarizes himself with Lewkowitsch, so that he does not need to use the index, can report analyses that are nearer the truth than deductions based upon the superintendent's nose, or the salesman's taste. It is not the purpose of this article to discuss oil analysis at length, but to express an opinion on the methods of oil analysis published as provisional by the American Leather Chemists Association. Probably few of these methods are used, and their defects are known to the members of the association, but that is no excuse for their existence and publication. Taking the methods in order, first comes

SAPONIFICATION VALUE.

It is of so little importance to a leather trade chemist, that most any method will answer the purpose, and the published method is a common one and very good. Saponification Value is of most importance in connection with such oils as rape seed oil, which has a low saponification value for a vegetable oil, and cocoanut oil, which has a high saponification value. It is used by some chemists as a quick method to determine the unsaponifiable in an oil, but the determination of the unsaponifiable by some sensible and quick method is more accurate. As a constant for detecting adulteration in cod and menhaden oils, the saponification value is worthless, and this applies to all oils used in the leather trade.

ACID VALUE.

This method might be improved, if it directed the weighing out of 2 or 3 grams of material in an Erlemeyer flask, and the addition of 25 cc. neutralized alcohol and ether-solution. Ether simply makes the end point more distinct, and it might be omitted.

The mixture of fat with alcohol and ether should be warmed a few minutes on a water-bath, or steam oven, before titrating, and instead of tenth normal alcoholic KOH, it is better to use tenth normal NaOH in aqueous solution. Alcoholic KOH is

Digitized by Google

inaccurate, and NaOH is more commonly used for standard solutions. The determination of free fatty acid and acid value could be developed into an accurate method in which different chemists should agree within 0.10 per cent.

IODINE VALUE.

So much research work has been done in developing the present methods of determining iodine value, that leather chemists can add very little to it, and the Hanus method should be satisfactory. Its definite wording, and rapidity and ease of execution tend to close agreement in results by the individual, or any number of chemists. As a rule the Hanus method gives results two or three points higher than those obtained by the Hübl method, and chemists in reporting results should state which method was used. Iodine value is growing more important commercially, and it is found in the specifications for many oils at the present time. It seems hardly possible that different chemists could disagree very much on iodine value of the same sample, but it is an actual fact that three well known members of this association analyzed the same sample of cod oil during the last year, and reported iodine values of 89, 140, and 156. To make matters worse, the man who reported 140 iodine value used his result to show that the oil contained a large amount of menhaden oil on account of the low iodine value. In Lewkowitsch there are tables, showing that menhaden oil has a lower iodine value than cod oil (Vol. 1, page 326), but an experienced American leather trade chemist should know that the chemical constants for cod and menhaden oils given in Lewkowitsch are absolutely worthless in considering American oils.

Pure menhaden oil will almost invariably give an iodine value ten or twenty points higher than pure cod oil. The Hanus method should be made official, and samples of the same oil should be sent out to the leather trade chemists to ascertain how closely they can agree on iodine value.

UNSAPONIFIABLE MATTER.

The method directs "wherever possible use the following method" and then leaves the chemist the option of trying several impossible things, or inventing another method. Probably a

Digitized by Google

50 per cent. by weight aqueous KOH solution is meant, instead of a 50 per cent. by volume solution, and this change is necessary. The method of saponification is tedious and incomplete, and the addition of sodium bicarbonate, with final extraction from sand in a Soxhlet extractor is a nuisance and does not accomplish the purpose intended. More soap is dissolved in the ether this way than by any other process.

The second method of saponification and extraction with ether by rubbing it in the soap is crude and amateurish and not worth considering. Methods like these might appeal to some college professor, who would charge about $50 for an analysis, the accuracy of which would be inversely proportional to the charge. The A. L. C. A. need some practicable method of determining unsaponifiable that will be generally used. In Lewkowitsch and Gill we see reference to methods of saponification with alcoholic KOH by boiling in a flask, and subsequent extraction of the unsaponifiable with petroleum, or sulphuric ether in a separatory funnel. A method might be developed from the following, which is used by several leather chemists to-day. Weigh 5 or 6 grams of sample into a 250 cc Erlemeyer flask, add 10 cc. of 50 per cent. by weight aqueous KOH, and 40 cc. alcohol. Connect with reflux condenser, twelve inch inner tube with bulbs preferred, and boil over bunsen burner for one or two hours, with occasional shaking. In case of a solid fat use 20 cc. of petroleum ether along with the potash and alcohol to dissolve the fat and insure complete saponification. This method will saponify oils and fats completely, but in order to satisfy the more fastidious, the solution after boiling could be evaporated on a water-bath with stirring. Wool grease products will be saponified sufficiently this way. The soap solution, paste, or whatever is obtained is washed with a small amount of hot water, about 50 cc., into a 500 cc. pear shaped separatory funnel, and cooled to room temperature. It is then shaken out three times with petroleum or sulphuric ether, using 50 cc. ether each time and shaking about five minutes. Alcohol and water can be used to break emulsions. For some fats the volume of solution in the separatory funnel must be made to 300 cc. with water to dissolve the soap. The combined ether solutions of the unsaponi-

Digitized by Google

fiable are washed in a separatory funnel with water and neutral alcohol, until all soap is washed out. This can be done in three to five washings. The ether solution is finally transferred to a clean dry beaker on water-bath, or in steam oven a few minutes to separate water. It is then poured into a dry weighed No. 1 beaker and evaporated to constant weight. A few hours in a steam oven will answer. It is very important to wash all of the soap out of the ether solution, as some chemists determine considerable soap in the unsaponifiable of moellons and report it as wool grease, unsaponifiable. The unsaponifiable residue can be burned to an ash, and the soap found by multiplying the ash by 10. Whether petroleum ether or sulphuric ether is used might be stated in the report. For every fat and oil, except those containing wool grease, petroleum ether boiling at 70° C. is satisfactory, and in most of the latter it will answer the purpose, but in the case of pure wool grease, sulphuric ether gives more unsaponifiable due to more complete solution of the cholesterol. In the case of twenty different samples of wool grease from as many different sources, which were analyzed recently using both kinds of ether, the unsaponifiable with petroleum ether averaged 34 per cent., and with sulphuric ether 42 per cent. Saponification in a flask for one hour gave the same unsaponifiable as saponification for twenty hours, and saponification under pressure gave only one per cent. less unsaponifiable than either of these methods.

MAUMENÉ TEST.

This test is not of sufficient importance to invite discussion. Iodine value is more accurate and serves the same purpose.

SPECIFIC GRAVITY.

This is an important test and should be determined as accurately as possible to the fourth decimal place. Pure oils of the same group seldom vary in gravity more than one or two points in the third decimal place, and this is well known by sophisticators.

A uniform way of determining specific gravity might be adopted, but the Westphal balance, or specific gravity bottle with thermometer and capillary overflow are very accurate.

Digitized by Google

It would seem that for the sake of uniformity, results should be reported as specific gravity at 15.5° C.

TITRE TEST.

The method published is a common reliable one.

MELTING POINT.

This is a tedious way of making a very simple determination. It requires too much time and chemists have been known to get two melting points 10° F. apart on the same sample by this method, owing to the indefinite end point at which the thermometer must be read. Wiley's method is more accurate and gives fairly good results. A quick and accurate method, which may be considered too simple and radical, can be found in the book on "Oil Analysis" by Geo. H. Hurst. Into a small glass capillary tube about 2 mm. in diameter the melted fat is drawn to a distance of about 10 mm. and allowed to cool for an hour, or over night. If it is cooled immediately under the hydrant, the melting point will be the same. The tube is fastened to a thermometer with rubber elastic, so that the fat is level with the mercury bulb, and then suspended in a beaker of water over a small burner. The temperature is raised slowly, and when the fat melts and becomes clear, the water forces it up the capillary tube. This occurs immediately when the fat melts and the end point is very distinct. This method gives duplicates within a half degree and works well with all greases, but for paraffin, it is better to determine the solidification point by the English method given in Lewkowitsch. It is easy and very accurate.

COLD TEST.

This method is absolutely worthless, because it states that the oil must be left one hour in the freezing mixture. The older methods stated that the oil was to be left in the freezing mixture until solid, and then stirred and the bottle inverted until the oil flowed. This method gave more uniform results than freezing for one hour, because after an oil has been frozen for an hour at variable temperatures, it is difficult to break it up with the thermometer and note the point at which it flows. Different oils, such as neatsfoot work differently under this treatment and it is a fact that some neatsfoot oils, after an hour's freezing give

Digitized by Google

a cold test higher than the cloud test. This method might be changed to freezing for five minutes at a definite temperature, or else abolished.

CLOUD TEST.

This is of more value than cold test under present conditions, and gives concordant results. Many oil dealers prefer it for that reason, and the method as published is satisfactory.

It has been suggested at different times that this association devise standard methods for the analysis of moellon, sod oil, etc., but the importance of the analysis of these materials has not justified it. Their analysis is not a difficult matter, except in the determination of wool grease, and that is a subject in itself. An accurate method for determining wool grease could be worked out from the cholesterol acetate, or acetic anhydride method, but no present method is reliable.

Methods for moisture, iodine value, unsaponifiable, free, fatty acid, etc., in moellons might readily be adopted, but there is some difference of opinion about degras former. A method such as Procter describes in his L. I. L. B. with the use of a little common sense will determine degras former. The soap solution from the unsaponifiable is used for the determination. The importance of degras former has been over-estimated and it is seldom taken seriously outside of France, Bohemia, and Milwaukee. A moellon containing 5 per cent. degras former will often work better in practice than one containing 12 per cent. The way the moellon is made and what it is made of are more important than the chemical tests that are given preference.

Instead of applying special tests like color tests for determining the purity of certain oils, it would be better to make specifications for gravity, iodine value, etc.

The subject of mineral oil analysis has been treated thoroughly by the chairman, Mr. Oberfell, and the methods mentioned are up-to-date and practicable. A committee should be appointed to revise the methods of oil analysis published by this association or abolish them, and leave the matter to the chemist's choice.

Digitized by Google

THE USE OF OIL OF MUSTARD AS AN ANTISEPTIC TO PREVENT THE DECOMPOSITION OF TAN LIQUORS.

By J. M. Seltzer.

The fact is well known that tan liquors rapidly deteriorate when kept for any length of time, and unless some suitable antiseptic is added they cannot be kept in their original condition. The best antiseptic which we have been able to find is "Artificial Oil of Mustard," and when used in the proportion of $^1/_{20}$ per cent. will preserve liquors almost indefinitely. The addition of this preservative is very simple since it mixes with the liquor at once and the number of drops to a given weight of the oil can be easily determined, and measured into the samples with a small bulb pipette.

In the collection of our tannery samples equal amounts are daily placed into large bottles which are kept well corked, and to each bottle enough oil of mustard is added to equal $^1/_{20}$ per cent. of the liquor that will be gathered during the period of collection. I have therefore made my experiments, which will follow, in closed bottles so as to represent conditions the same as they are in the collection of the samples in the tannery.

Oil of mustard was used by others in research work to find a suitable antiseptic for the preservation of tan liquors and was found to be unsatisfactory. One of the investigators placed samples treated with $^1/_{20}$ per cent. of this preservative in an incubator at a constant temperature of 30 degrees C. for 10 days and found that they did not hold the acid. The writer thinks that this test was too severe to determine its value as an antiseptic, since oil of mustard is quite volatile and when samples treated with it are kept in open vessels, even at ordinary temperatures, its strength is soon dissipated into the air and the preservative powers are lost.

The following liquors, all of which are 35 degrees barkometer, were made up and left standing in a warm room for 4 months. The temperature ranged from 20 degrees C. to 28 degrees C. and the solutions were kept in closed bottles.

Digitized by Google

DETERMINATION OF ACID AS ACETIC.

Kind liquor	Start per cent.	After standing 4 months per cent.
Pure hemlock bark	0.14	0.13
Pure mangrove bark	0.08	0.08
Pure oak bark	0.22	0.20
Liquid chestnut oak extract	0.42	0.46
Solid chestnut oak extract, No. 1	0.62	0.68
Solid chestnut oak extract, No. 2	0.60	0.60
Liquid quebracho	0.10	0.09

1/20 per cent. oil of mustard was added to each of the above liquors.

LIQUOR NO. 1.

Sapped liquor; barkometer 40¼°. Temperature during all of the following experiments was from 20°C. to 26°C. Determination of acid as acetic.

Preservative added	No preservative Per cent.	1/20% oil of mustard Per cent.	1/20% thymol Per cent.
Start	0.57	0.57	0.57
After standing—			
1 week	0.54	0.58	0.59
2 weeks	0.45	0.58	0.66
3 weeks	0.44	0.58	0.72
4 weeks	0.42	0.58	0.72
5 weeks	0.42	0.59	0.74
8 weeks	0.40	0.56	0.70

ANALYSIS OF LIQUOR NO. 1.

	Start	After standing 5 weeks		
Preservative added	No preservative	No preservative	1/20% oil of mustard	1/20% thymol
Barkometer	40¼°	39½°	40¼°	40¼°
Total solids	9.41%	—	9.38%	9.44%
Soluble solids	9.27	9.14	9.27	9.27
Insolubles	0.14	—	0.11	0.17
Non-tannins	5.17	5.07	5.14	5.14
Tannins	4.10	4.07	4.13	4.13

LIQUOR NO. 2.

Same as No. 1, except that 0.42 per cent. acetic acid was added. Determination of acid as acetic.

Preservative added	No preservative Per cent.	1/20% oil of mustard Per cent.	1/20% thymol Per cent.
Start	0.99	0.99	0.99
After standing –			
1 week	0.97	1.00	1.00
2 weeks	0.79	1.00	1.02
3 weeks	0.79	1.01	1.07
4 weeks	0.76	1.00	1.12
5 weeks	0.75	1.04	1.20
8 weeks	0.64	0.99	1.07

Digitized by Google

ANALYSIS OF LIQUOR NO. 2.

Preservative added	Start: No preservative	After standing 5 weeks: No preservative	After standing 5 weeks: 1/20 % oil of mustard	After standing 5 weeks: 1/20 % thymol
Barkometer.....	40½°	40°	40½°	40½°
Total solids.....	9.41%	—	9.35%	9.40%
Soluble solids....	9.25	9.22	9.24	9.26
Insolubles	0.16	—	0.11	0.14
Non-tannins	5.12	5.14	5.13	5.11
Tannins	4.13	4.08	4.11	4.15

LIQUOR NO. 3.

Sapped liquor; barkometer 25¼°. Determination of acid as acetic.

Preservative added	No preservative Per cent.	1/20 % oil of mustard Per cent.	1/20 % thymol Per cent.
Start	0.30	0.30	0.30
After standing—			
1 week	0.52	0.32	0.30
2 weeks	0.60	0.36	0.32
3 weeks	0.63	0.36	0.30
4 weeks	0.58	0.34	0.26

ANALYSIS OF LIQUOR NO. 3.

Preservative added	Start: No preservative	After standing 4 weeks: No preservative	After standing 4 weeks: 1/20 % oil of mustard	After standing 4 weeks: 1/20 % thymol
Barkometer.....	25¾°	24°	25½°	25½°
Total solids.....	5.94%	—	5.80%	5.81%
Soluble solids....	5.81	5.31	5.67	5.66
Insolubles	0.13	—	0.13	0.15
Non-tannins	4.58	4.02	4.40	4.47
Tannins	1.23	1.29	1.27	1.19

LIQUOR NO. 4.

Fresh liquor; barkometer 45½°.

Preservative added	No preservative Per cent.	1/20 % oil of mustard Per cent.	1/20 % thymol Per cent.
Start	0.54	0.54	0.54
After standing—			
1 week	0.44	0.54	0.56
2 weeks	0.26	0.54	0.56
3 weeks	0.22	0.54	0.58
4 weeks	0.22	0.54	0.58

Digitized by Google

ANALYSIS OF LIQUOR NO. 4.

Preservative added	Start: No preservative	After standing 4 weeks: No preservative	After standing 4 weeks: 1/20 % oil of mustard	After standing 4 weeks: 1/20 % thymol
Barkometer.....	45½°	40½°	45½°	45½°
Total solids.....	10.20%	—	10.27%	10.34%
Soluble solids....	9.95	8.71	9.81	9.84
Insolubles	0.25	—	0.46	0.50
Non-tannins	4.68	4.01	4.58	4.64
Tannins	5.27	4.70	5.23	5.20

In every case where no preservative was added to the liquors, a thick "mother" formed and it was impossible to accurately determine the total solids of them. In the liquors to which oil of mustard, and thymol, had been added, no noticeable change took place. The writer regrets that he did not analyze the liquors to which thymol had been added, at the commencement of the experiment, since 0.05 per cent. of solid matter was introduced into each one by the addition of that preservative. This accounts for the percentages being somewhat higher in these liquors over those to which oil of mustard had been added.

While the tannin analysis of the liquors treated with oil of mustard and those treated with thymol do not materially differ, the ones treated with the latter certainly do not hold their acid, and it is evident that some lactic fermentation has taken place.

In conclusion I must say that we have found oil of mustard to give excellent results in our practical work and I know of others who use this preservative and will bear me out in these statements.

NOTES ON THE DETERMINATION OF FREE SULPHURIC ACID IN LEATHER.[1]

By Edmund Stiasny and C. D. Wilkinson.

The exact determination of free sulphuric acid has been a subject for frequent investigations, and though we know a good number of methods proposed for this purpose, none of them can be said to be wholly satisfactory[2]; any new method therefore deserves the interest of the leather trades chemist and of

[1] *Collegium*, 507, 294-8.

[2] See H. R. Procter, Leather Industries Laboratory Book, p. 366-373.

Digitized by Google

the leather manufacturer as well, as the presence of free sulphuric acid is generally acknowledged to have a detrimental effect on the leather.

The method recently published by B. Kohnstein[1] does not seem to have advantages over the methods hitherto known; it consists in extracting the fine leather cuttings repeatedly with a strong solution of magnesium bicarbonate, using a separating funnel, and making up the solution to 250 c. c. Free sulphuric acid will react with the magnesium bicarbonate according to the following equation:

$$H_2SO_4+MgH_2(CO_3)_2=MgSO_4+2CO_2+2H_2O.$$

The magnesium sulphate thus formed is determined in the ordinary way after removing the excess of magnesium bicarbonate and any organic magnesium salt by boiling, evaporating and igniting.

The figures which Kohnstein obtained by this method show good concordance with the figures he expected, and though the magnesia estimation renders the whole method a rather elaborate one, we thought it might still form a valuable addition to our present methods. Still there were points which we thought required further elucidation before the method could be adopted for all practical cases. One was, that barium chloride present in the leather would react with magnesium bicarbonate, and the magnesium chloride so formed would but partially be converted into magnesium hydrate by repeatedly evaporating and igniting. This case would not, however, be of serious importance as one need not test for free sulphuric acid in leather after having found soluble barium salts present.

The other case in which one would expect, the method to fail on theoretical grounds is the presence of free sulphuric acid together with any soluble chlorides in the leather. In this case the magnesium sulphate formed and the chlorides extracted would on evaporating and igniting form magnesium hydroxide so that the figure of soluble magnesium salts finally obtained and calculated as free sulphuric acid would be found considerably too low.

The experiments which we made in order to prove our an-

[1] *Collegium*, 1911, p. 314.

Digitized by Google

ticipations have further on convinced us that the method, even in absence of barium chloride or other chlorides gives much lower results than the method of Procter and Searle (which by the way is known to give rather too low than too high figures); and the reason for these unsatisfactory results with the new method was found to be the difficulty of completely extracting the free sulphuric acid from the leather by means of magnesium bicarbonate. To prove the above statements the following experiments may be quoted:

I. The influence of barium chloride on the method.

It was supposed that the barium chloride will react with the magnesium bicarbonate according to the equation:

$$BaCl_2+MgH_2(CO_3)_2=BaCO_3+MgCl_2+CO_2+H_2O$$

and that the magnesium chloride in the subsequent processes of evaporating and igniting is only partially converted into insoluble magnesium hydrate

$$MgCl_2+2H_2O=Mg(OH)_2=2HCl.$$

The remaining part of soluble magnesium chloride will then be determined as if it were magnesium sulphate and calculated as free sulphuric acid.

(a) Experiment, showing the behavior of a mixture of $BaCl_2$ and $MgH_2(CO_3)_2$ when treating the solution according to Kohnstein's method.

Ten cubic centimeters of a 1 per cent. barium chloride solution were shaken with 100 cubic centimeters of a fairly strong solution of magnesium bicarbonate and subsequently treated according to the prescription of Kohnstein's method. The weight of $Mg_2P_2O_7$ was found to be 6.7. mg. and this when calculated as free sulphuric acid amounts to 5.9 mg. H_2SO_4.

(b) Experiment showing the effect of $BaCl_2$ present in leather on the results obtained by Kohnstein's method.

Thirty g. of a leather containing about 23 per cent. barium chloride were treated according to this method. Fifty cubic centimeters of the filtrate (from 250 cubic centimeters of the total volume) gave, though twice ignited 0.2898 g. $Mg_2P_2O_7$ which corresponds to 4.26 per cent. free sulphuric acid. A duplicate determination gave 0.3094. $Mg_2P_2O_7$ corresponding to 4.55

Digitized by Google

per cent. free sulphuric acid. (It depends on the special working conditions, if more or less magnesium chloride is converted into magnesium hydrate, hence the difference in the results.)

Thus more than 4 per cent. free sulphuric acid was found, although the leather was obviously quite free from it.

II. The influence of alkaline and other chlorides on the method.

If sodium chloride is present in a leather together with free sulphuric acid, the solution obtained by shaking the leather with a magnesium bicarbonate solution will contain both salt and magnesium sulphate. Such a mixture will behave like sodium sulphate and magnesium chloride, when it is evaporated, dried and ignited. The magnesium chloride will be partially converted into insoluble magnesium hydrate, the total effect being expressed by the following equation:

$$MgSO_4+2NaCl+H_2O=Mg(OH)_2+Na_2SO_4+2HCl.$$

This means a loss of magnesium and a value for free sulphuric acid much lower than would be found in absence of salt.

(a) Experiment showing behavior of a mixture of magnesium sulphate and sodium chloride, when treating the solution according to Kohnstein's method.

A magnesium sulphate solution about 1 per cent. was made and 25 cubic centimeters of this solution mixed with 10 cubic centimeters sodium chloride solution (10 per cent.), evaporated, dried, ignited and the magnesia determined in the water soluble part of the residue (a part was insoluble magnesium hydrate). 0.0771 g $Mg_2P_2O_7$ were weighed corresponding to 0.016 $MgSO_4.7H_2O$. A parallel test with 25 cubic centimeters of the original magnesium sulphate solution(without the addition of salt) gave 0.1130 g $Mg_2P_2O_7$ corresponding to 0.236 g $MgSO_47H_2O$. This shows that by the presence of salt only 68 per cent. of the magnesium sulphate was determined.

(b) Experiment showing the effect of salt present in leather on the results obtained by Kohnstein's method.

Eighty g of small leather shavings (containing no free sulphuric acid) were treated with a solution of 20 g of common salt in 400 cubic centimeters of about $N/10H_2SO_4$ and the leather collected in a funnel, air dried, and then well mixed and kept in a stoppered bottle. Another portion of the leather was treated

Digitized by Google

similarly with H_2SO_4 (without salt). Both samplies were analysed according to Kohnstein's method with the result stated in Table I[1], showing that the presence of NaCl very much lowers the figures for H_2SO_4. This proves that the anticipation of chlorides effecting the correctness of the method was sound. The table also contains the figures obtained when the two leathers were analyzed according to the well known method of Procter and Searle. Here we find a striking divergence between the results obtained by the two methods. The Kohnstein figures for the leather containing free sulphuric acid without salt is but 47 per cent. of the Pocter and Searle figure, and for the leather containing free sulphuric acid together with salt only 12 per cent. of the correct value (according to Procter and Searle).

TABLE I.

	Free H_2SO_4 found by Kohnstein's method per cent.		Free H_2SO_4 found by Procter-Searle's method per cent.		Ratio of Kohnstein figure to Procter-Searle figure per cent.
I. Leather containing no free H_2SO_4 but much $BaCl_2$	4.26	4.55	no free H_2SO_4 to be expected		—
II. Leather containing free H_2SO_4 and NaCl	0.16	0.17	1.34	1.35	12
III. Leather containing free H_2SO_4	0.58	0.58	1.22	1.24	47

This shows that even in absence of salt the result was quite unsatisfactory and that there was a serious fault either in our way of carrying out Kohnstein's method, or in the method itself; we tried to find out the reason for these differences, starting with the extraction method by means of $MgH_2(CO_3)_2$ which we suspected to be incomplete.

Thirty g of a leather, containing free sulphuric acid was cut into small shavings (the size as recommended by Kohnstein) and shaken out with a $MgH_2(CO_3)_2$ solution in the prescribed way. After having collected 250 cubic centimeters of the extracted solution, the extraction was continued until a second 250 cubic centimeters flask was filled, and then continued again until a third 250 cubic centimeters of extract solution was obtained. These three extractions (I, II, III) were analyzed separately according

[1] This table also contains some of the results previously mentioned.

Digitized by Google

to the method. If the extraction was complete with the first 250 cubic centimeters we ought not to have found any more $MgSO_4$ in the II and III portion. The figures (see Table II) show that

TABLE II.

	Free H_2SO_4 found by Kohnstein's method per cent.		Free H_2SO_4 found by Procter-Searle's method Per cent.	
1. Extraction	0.42	0.40	—	—
2. Extraction	0.09	0.10	—	—
3. Extraction	0.085	0.09	—	—
Total	0.595	0.59	1.17	1.18

this was not the case, and that repeated extraction will remove continuously new amounts of sulphuric acid. The comparison of these figures with the figures obtained by the Procter-Searle method clearly show that the three times extracting only removed one half of the total free sulphuric acid out of the leather.

Concluding, we are forced to state that we have not been able to get satisfactory results with Kohnstein's method, and that this method will, apart from the difficulty of completely extracting the free sulphuric acid, fail on theoretical grounds if any chlorides are present in the leather.

Some few remarks may be made as to another method of determining free sulphuric acid which was proposed by Wünsch[1] and simultaneously by one of us[2] which is based on the oxidation of the leather with fuming nitric acid. This method requires a correction for the sulphur present in the hide substance which is oxidized to sulphuric acid and which is equivalent to 0.25 per cent. of the hide substance (or 1.4 per cent of the nitrogen found in the leather).

Several leathers showed by treatment with nitric acid much less sulphur than was to be expected even if no sulphates or sulphuric acid were present. This makes it probable that oxidizing with fuming nitric acid does not convert all the sulphur of hide-substance into sulphuric acid. In fact it has been shown by Moerner in the case of pure gelatin containing 0.25 per cent. sulphur, that this gelatine by oxidizing with fuming nitric acid only gave 0.012 per cent. sulphur, and with strong nitric acid 0.019

[1] **Wissenschaftliche Beilage des Ledermarkt, 1901, p. 141.**

[2] *Der Gerber*, 1901, p. 235.

Digitized by Google

per cent. sulphur, with aqua regia 0.018 per cent. sulphur. That is, only 4.8—7.6 per cent of the expected amount has been found, the most part of sulphur being oxidized to CH_3SO_3H which gives no insoluble barium salt.

It may therefore be recommended, not to make any allowance for the sulphur in hide-substance, if the oxidation-method with nitric acid is used.

THE SOAKING OF DRIED HIDES BY MEANS OF FORMIC ACID.[1]

By J. R. Blockey, M.Sc.

The following experiments on the use of formic acid in soaking dried hides were suggested by the method of anthrax sterilization recently proposed by Mr. A. Seymour-Jones. This method of sterilization consists of the use of formic acid and mercuric chloride on the raw hides, by which it is claimed that all anthrax spores are effectively killed.

As is well known, the great difficulty with dried hides is in the soaking. It is the object of soaking to bring the hide back as closely as possible to its original condition when immediately taken from the animal's back.

With a fresh market hide this condition is scarcely changed during the short interval of time before the tanner gets it, and all that is then necessary to do is to wash off the extraneous blood and dirt. With dried hides the conditions are very different. If the drying is done slowly, and at low temperatures, then the main change which takes place is that moisture evaporates from the hide, leaving the fibers still separated from one another and not altered chemically. The object or function of drying being merely, to get the hide in such a condition that it will not putrefy, all that is necessary for this is the removal of moisture, since putrefactive and decomposition processes require moisture before they can proceed. If no moisture be present no putrefaction will take place. Theoretically this is all that is required to preserve hides by drying, but in practice these limits are often over-stepped, and instead of mere removal of moisture, leaving

[1] Tanners' Year Book, 1912, pp. 98-105.

Digitized by Google

the fibers chemically unaltered, it is very common for the fibers to be dehydrated; that is, through excessive temperatures in drying, the fibers have become chemically altered, losing water of combination; and also the fibers have cohered together, producing the effect of unorganized or structureless tissue.

In the soaking back of the hide the original condition is restored fairly readily if the fibers have not been chemically dehydrated; but it, through too high temperatures in drying, the fibers have cohered together, then the soaking back is a very difficult and tedious operation, and recourse must usually be had to chemicals to soften the hides. In this soaking back, which often takes considerable time, using stale soaks and chemicals, much hide substance is usually lost, and it is one of the chief drawbacks of dried hides that quite a considerable quantity of hide substance must, as a rule, be lost before the hides assume a sufficiently soft condition to proceed to the limes. It was partly the object of the following experiments to see if, by the use of formic acid, the amount of hide substance lost in the soaks could be diminished.

In the first series of tests, ten dried Central American hides were taken and thrown into clean water for a day, then taken out and divided into two packs. One pack was put in a one-half per cent. sodium sulphide liquor, and the other pack suspended in a 1 per cent. solution of formic acid. Next day the hides were hauled. The formic acid one were very swollen compared with the sulphide ones, and the strength of the acid had gone down to one-eighth per cent. The strength of the acid was brought up again to one-half per cent. and the hides put back. On the next day the formic acid ones were very swollen and quite rubbery, and the acid had gone down to one-quarter per cent.

Both packs were drummed for two hours, after which the hides felt much softer, and they were then put into clean water where they remained until the following day, when they were again drummed and put back in fresh water. This hauling and drumming for an hour or so in running water was repeated for two more days, that is, until the hides had been in the soaks for seven days. By this time the sulphide ones were quite soft

Digitized by Google

enough to go to limes, whilst the acid ones still felt swollen and "boney." However, they were all drawn into limes and given the usual liming of twelve days by the three-pit system. After liming, the hides felt very plump, and the formic ones much more so than the others. Unhairing and fleshing were not more difficult with the acid ones than with the others. The percentage of pelt weight on the green weight was 230 for the sulphide ones and 236 for the formic acid ones. After de-liming with boracic acid, they were tanned in the usual way, the formic ones all the time feeling plumper and firmer than the sulphide ones, but with a slight tendency to harsh grain.

Second series, using one-half per cent. formic acid. The next hides used were dried Madagascars of an average of 21 pounds. After washing for two days in clean water, they were divided into two packs, one pack being softened as before with a one-half per cent. sulphide solution, and the other pack with one-half formic acid. After one day's soaking the formic acid ones were much more swollen than the sulphide ones, but not as swollen as the previous ones when 1 per cent. of acid was used. On the second day of soaking they were drummed for two hours in running water, and again on the third and fourth days. By this time the formic ones were much more swoolen than the others, and quite firm. After five days' chemical soaking, that is after seven days total soaking, they were drawn into limes and limed in the usual way for twelve days.

The rounding table figures gave 223 per cent. for the sulphide ones on the green weight, and 226 per cent of the formic ones.

Third series, using one-quarter per cent. formic acid. A third series was performed using a one-quarter per cent. solution of formic acid, instead of one-half per cent. or 1 per cent. as before. The hides were dried Central Americans, averaging 28 pounds. A parallel pack was softened with sulphide as before. To prevent the excessive swelling of the hides by the acid, an addition of one-half per cent. salt was made. The swelling was scarcely at all prevented, so that after three days in the acid the amount of salt was brought up to 2 per cent. This resulted in reducing the swelling, and the hides then seemed in an admirable condition as regards softness and pliability. After

Digitized by Google

drumming in running water the swelling again became apparent by the usual depickling action of water. After five days soaking they were put into limes and limed for ten days. The rounding table weights worked out as follows:—

Formic ones	239 per cent.
Sulphide ones	234 per cent.

Fourth series, using one-quarter per cent. of formic acid. The hides for this series were dried Central Americans, averaging 28 pounds. After soaking for two days in clean water, half of them were soaked in a one-quarter per cent. solution of caustic soda and the other half in one-quarter per cent. formic acid. In this case, to prevent swelling, the salt—2 per cent.—was added along with the acid before the hides were put in, and no drumming at all was given. The acid ones did not swell as much as before, and in fact not as much as the caustic soda ones. After soaking for five days they were all drawn into limes and given nine day's liming.

The rounding table weights were as follows:—

Formic ones	226 per cent.
Caustic soda ones	219 per cent.

EXPERIMENTS WITH SOLUTIONS OF ONE-TENTH PER CENT. OF FORMIC ACID.

On account of the excessive swelling which is liable to take place, and the cost of using solutions of concentrations higher than one-quarter per cent., it was thought that more dilute solutions would be more convenient and economical, and experiments were therefore carried out with liquors of one-tenth per cent. formic acid. The method which has been found to be most satisfactory was similar to that described above. The hides were thrown into clean water for one or two days to render them sufficiently soft to open out, and were then suspended in the formic acid solution. (By suspension, better and more uniform results are obtained than by laying them flat in the pit, although, of course, the volume of liquor required is greater). The softening effect was the same as with the greater strengths, and the swelling effects were not so pronounced. During the suspension the hides should be hauled up and allowed to lie in a pile once a day. After two or three days in the liquor,

Digitized by Google

the hides are usually soft enough to be drummed. The drumming should not be too violent or too prolonged; about half an hour in a slowly revolving drum with a little water being quite enough. The hides should be drummed once a day for two or three days until thoroughly softened. At the end of this time they will be in a fit condition to go to the limes, the whole process of soaking taking from five to seven days. Not only is the softening effect produced by the one-tenth per cent. solution, but the amount of acid absorbed by the hides is much less (See table D.)

It seems, therefore, preferable from the point of view of economy and efficiency to use a strength of one-tenth per cent. than the solutions of higher concentrations.

LOSS OF HIDE SUBSTANCE.

To estimate the amount of hide substance lost in the course of soaking, samples of the liquor were taken at every stage, and the amount of dissolved hide substance determined by nitrogen estimation. The following tables show the results:—

HIDE SUBSTANCE LOST IN SOAKS.

First Series.

In fresh soak for 2 days		In 1% formic acid for 5 days		In ½% sulphide for 5 days	
Grams hide substance per 100 cc.	Lbs. hide substance per 100 lbs. hide	Grams hide substance per 100 cc.	Lbs. hide substance per 100 lbs. hide	Grams hide substance per 100 cc.	Lbs. hide substance per 100 lbs. hide
0.11	1.0	0.01	0.02	0.062	1.2

Third Series.

Hides in fresh water for 2 days			Hids in 1 day		Hides in 3 days		Hides in 5 days	
Grams h. s. per 100 cc.	Lbs. h. s. per 100 lbs. hide		Grams h. s. per 100 cc.	Lbs. h. s. per 100 lbs. hide	Grams h. s. per 100 cc.	Lbs. h. s. per 100 lbs. hide	Grams h. s. per 100 cc.	Lbs. h. s. per 100 lbs. hide
0.061	0.5	formic acid ¼%	0.0105	0.2	0.016	0.32	0.016	0.32
		sulphide ½%	0.0123	0.25	0.021	0.40	0.031	0.62

Fourth Series.

Hides in fresh water 2 days			Hides in 1 day		Hides in 5 days	
Grams h.s. per 100 cc.	Lbs. h.s. per 100 lbs. hide		Grams h.s. per 100 cc.	Lbs. h.s. per 100 lbs. hide	Grams h.s. per 100 cc.	Lbs h.s. per 100 lbs. hide
0.053	0.46	formic acid ¼% salt 2%	0.005	0.10	0.013	0.26
		caustic salt ¼%	0.013	0.26	0.032	0.64

Digitized by Google

HIDE SUBSTANCE LOST IN DRUMMING.

In order to see if hide substances were lost in the drumming, samples of the drum liquor were taken and analyzed. The samples were taken after equal intervals of time, using the same volume of water in each case. The filtered solutions were used:—

	Grams. h. s. per 100 ccs.
A. Formic acid soaking	0.0108
B. Sulphide soaking	0.043

A curious result was obtained with the formic acid liquor collected from the drum. After allowing this liquor to stand for a short time, a heavy precipitate was seen to settle on the bottom of the jar, and on investigation it proved to be almost pure hide substance, the amount being lost after this drumming being approximately one-half pound per 100 pounds of hide. No such precipitate was observed with the sulphide drum liquor.

ABSORPTION OF ACID.

The following tables show how the acid was absorbed by the hides:—

A. USING 1 PER CENT. OF ACID.

	Original solution	After 1 day
Per cent. of acid in the liquor	1.0	0.15

B. USING ONE-FOURTH PER CENT. OF ACID.

	Original solution	After 1 day
Per cent. of acid in the liquor	0.25	0.10

C. USING ONE-FOURTH PER CENT. OF ACID AND 2 PER CENT. SALT.

	Original solution	After 1 day	After 3 days	After 5 days
Per cent. of acid in the liquor	0.25	0.21	0.20	0.18

D. USING ONE-TENTH PER CENT. ACID ALONE.

	Original solution	After 1 day	After 4 days
Per cent. of acid in the liquor	0.1	0.077	0.060

Showing a loss of 0.04 per cent.

The amount of acid required per hide (averaging 25 pounds in the dry state) works out at one-fifth of a pound, or less than a penny per hide, when working with one-tenth per cent. acid.

Since the liquor is antiseptic it can be used over again many times. When one pack has been through, the liquor should be

Digitized by Google

titrated with alkali, and the amount of acid which has been absorbed is then calculated and this quantity should then be added to the liquor to prepare it for the next pack.

The volume of liquor which is required with the above dilution is rather high, since the hides are suspended and not laid flat.

The usual volume of liquor in the above experiments was about 70-80 gallons per hide. The question of volume is an important one, and it may happen that when the volume of liquor required per hide is less than the above figure, the concentration of the acid should be higher in order to produce the best results.

NOTES ON THE LIMING OF HIDES WHICH HAVE BEEN SOFTENED IN FORMIC ACID.

Formic acid is a sterilizing agent and prevents bacterial action in the soaks. This effect also seems to be carried into the limes. The loosening of the hair takes place rather more slowly with hides which have been softened with formic acid than with those softened with alkali. The hides are probably sterilized when they go to the limes, and the bacterial action necessary for the loosening of the hair is somewhat retarded. The liming, therefore, is rather longer than usual, but this does not imply a greater loss of hide substance. This effect can be overcome by adding sodium sulphide to the limes. By the addition of sulphide to the limes the length of time required for complete loosening of the hair and swelling of the fibers can be reduced to the normal.

The appearance of the hides after liming, unhairing and fleshing is briefly as follows: They have not the same "pelty" soft feel of hides softened by alkali, but they are firmer. The increase of firmness shows itself on the rounding table; the shoulder and belly portions are thicker and firmer, and consequently the size of butt which can be cut off is greater and the percentage of butt weight on the total pelt weight is hgiher.

THE TANNING OF HIDES WHICH HAVE BEEN SOFTENED IN FORMIC ACID.

The appearance of the hides through the early liquors is rather different from the appearance of hides softened in alkaline soaks, mainly with regard to firmness. Throughout the whole process of tanning they are firmer than the others. The

Digitized by Google

penetration of the tan is approximately the same, and there is no difference in the color.

APPEARANCE AND WEIGHT OF THE FINISHED LEATHER.

The hides finished in the usual way, do not present any great difference as regards appearance, except with the firmness, which is still maintained in the finished leather. That is, the formic acid hides finished firmer and harder than the others. The color was the same. With regard to the weight of the leather obtained, there was a marked difference.

Since the percentage of limed pelt weight on the green weight is so much higher than with alkaline soaks, it might have been expected that the percentage of finished weight, calculated on the pelt weight, would not be as high with the formic acid softened hides as with the others, but the reverse is the case. Not only is the pelt weight higher when softened with formic acid, but also the percentage of finished weight on the pelt is higher, showing, therefore, a further total increase in the yield of leather from the raw material. With one pack of butts the percentage of finished weight on the pelt weight was 80 for the formic acid and 77.5 for the sulphide ones. Taking this into consideration along with the increase in the pelt yield with the formic acid, the total increase in finished leather from the raw material is very marked.

Leathersellers' Technical College,
176 Tower Bridge Road, S.E.

TANNERY SEWAGE DISPOSAL.[1]

By F. A. Loveland.

The time when the tanneries of the country can run the wastes from their works into streams raw and untreated is fast nearing an end, and in many localities the question of the nuisance arising from the common practice is already being taken up in various ways such as through the medium of the courts, by means of boards of health, live stock commissions, hunting and fishing clubs and so forth.

[1] Paper read at the Boston Meeting, National Association of Tanners July, 1912. Reprinted from Shoe and Leather Reporter of July 18, 1912.

Digitized by Google

For one tanner to congratulate himself that thus far he has escaped action or complaint against his tannery probably means that the community in which his works are located have been indulgent or apathetic, for sooner or later the broader action of the county or state will reach and embrace him, and make necessary that some means be provided for the disposition of his wastes other than dumping it into the streams unpurified.

There are probably few tanners who will claim that there is no reason for complaint against the ordinary method of tannery sewage being run direct from the works into the waters of the country in a raw state, for it is commonly known that a tannery is not a rose garden, and that under certain conditions odors might develop from its sewage which would be offensive to delicate nostrils, and possibly prove detrimental to the fish which live in the stream and to animals grazing along its banks and drinking the water therefrom.

Nor is it likely that any tanner would be so forgetful of his duty to his neighbors but that he would be glad to do anything within reason to purify and sweeten the liquid wastes from his plant, knowning that by so doing he would also make for better conditions for himself and workmen.

So far as conditions about the ordinary tanning plant are concerned, probably not much criticism can be made as to its not being kept in a sanitary state, for most tanners will undoubtedly concede that one of the essentials, for making a good product is clean and wholesome conditions in and about the plant.

Sometimes unjust criticism is made against necessary tannery odors, for there are odors about some industrial plants which are characteristic of the industry and cannot be avoided, like slaughter houses, rendering plants and fertilizer works, and about the tannery the smell of tanning liquors and hides and skins will probably always continue, and complaints about them are naturally beside the mark.

The successful treatment of tannery sewage presents a problem difficult to solve because of the character of the wastes. Where the sewage requires to be pumped in order to receive treatment, it is found that the pumps become easily and seriously clogged with the hair and flesh which find their way into the sewage, even

Digitized by Google

when great care is taken to prevent their entrance. The salt and dirt which is washed from the hides mixes with lime and hair, forming a sort of cement which is apt to obstruct the sewers carrying the sewage to the treating tanks.

Perhaps no tanner would own to wasting any considerable amount of his tannin, yet careful as he may be there is sufficient present in most tannery sewage to produce a dark color to the water into which the effluent flows, especially where traces of iron are present in the water.

Where a fine filtering media, like sand, is used, the lime soaps and fats present in the sewage and carried past the precipitation tanks, soon clog the pores of the filter and make it useless. Even though the effluent may be of fair character when it enters the stream, the soluble solids it contains soon decompose and deposit these solids in a light, flocculent form on the bottom and along the sides of the stream, making an unsightly appearance, and causing offensive odors in warm weather. Where precipitation tanks are installed it is found that the sludge is difficult to free from water so as to handle cheaply and quickly in the cleaning of the tanks, and in carting away.

It has also been claimed that tannery sewage when mixed with ordinary city sewage makes the whole more difficult of treatment in municipal treating works, an English tanner stating that he was imposed an additional tax for this reason, also because it was claimed that the character of his sewage was such as to cause a slow deterioration of the material of which the sewer was composed into which his effluent flowed. The foregoing are, perhaps, the chief items which go to make up the problem as a whole, though others may readily occur to some of you in connection with the problems of your individual plants.

Perhaps it would be of interest to note some of the methods in operation in plants where attempts are being made to purify the sewage. One large tannery has a series of four settling vats, built about three or four feet above grade, into which the sewage is pumped. These vats are built so as to be operated in series, and so arranged that any one can be cut out for cleaning while the others remain in operation. They are built above ground so the sludge can be readily loaded into a wagon-box from an open-

Digitized by Google

ing in the side of the vat being cleaned. From these vats the sewage goes to the stream.

Another tannery pumps the sewage to a high point of ground from whence it flows to the stream over a series of dams, thus allowing the solid matters to settle and collect in the pockets behind the dams. A resident near the tannery in describing this method said the odors were quite pronounced in the heat of summer, caused probably by the decay of putresible matters held back by the dams.

Another tannery had a large vat built in which was constructed a false bottom of heavy wire cloth. The sewage is run into this above the false bottom, and then pumped from below the wire screen into a tank or leach partly filled with spent bark, and after filtering through this medium is run to the stream.

Another method in use by a large tanner is to run the sewage on to filter beds about 30 feet x 5 feet deep made up of screened cinders. Several of these beds are laid down, so when one becomes obstructed it can be cut out, cleaned, redressed and made ready for service while others are in operation.

A method tried out by a large tanner having around a million gallons of daily sewage, was to construct a series of settling or precipitation vats, four in number, supplemented with a series of sand filters. The sewage was first run into the settling vats to deposit the hair, flesh, lime and other heavy solids; thence over the sand filter beds and to the stream. This method proved a failure in practice for it was found that the lime soaps and fats, carried past the settling vats, soon clogged the sand filters to such an extent as to make them useless. This part of the system was then abandoned and the settling vats alone retained in operation.

Another plant having about one hundred thousand gallons daily sewage has been under experimental work in connection with the health department of its state for some time and the following report from the state department may prove of interest as it bears directly on this question: "The state department of health has made investigations and experiments in co-operation with your company for the treatment of liquid wastes at your tannery. It appears that the solids in the waste at your tannery can be separated from the liquids at a reasonable cost. The

Digitized by Google

putrefactive bacteria can be destroyed by double filtration, the expense for installation and maintenance being very high.

"An acre of sand filter would be required and its cost would be approximately $15,000. The straining of the settled effluent would be necessary and a double pumping also. Probably the outlay for installation would not be less than $20,000. This process should filter out the anthrax germs, but not necessarily destroy them. They would be retained in the filter for indefinite periods.

"A stable effluent can be secured and all B. coli communis be destroyed by the use of chlorinated lime and the cost of doing this is within the means of your company. However, this will not kill the anthrax germ. After subsidence and straining through a rough filter, the effluent might be passed through a mechanical filter whose object would be to retain the anthrax spores. The waste wash water from cleaning operations would be small in bulk and could be evaporated in the boiler under 60 pounds pressure or more, which would assure the destruction of the spores. By this process, which would come within your means, and by the use of bleach a stable effluent would be secured, the colon would be destroyed and the anthrax germs would also be eliminated.

"The sludge should be reduced to dried, inflammable material by a centrifugal dryer and then destroyed by fire under the boilers, such as is the practice in a number of sewage disposal works in this and foreign countries.

"The straining or roughing filter between the subsidence tank and the sand filter would be small in area and might be economically built of porous asbestos. The advantage of this construction would be that the strained out materials could be subjected to combustion without removal from the layer of asbestos, by use of an overhead flame. In the tests conducted by the department and your company, where the treatment by the use of chlorinated lime of the whole waste of the tannery was accomplished, the odor of chlorine was detected for four miles below the tannery. The offensive odors along the stream, about which complaint has been made for several years, were thus effectively reduced.

Digitized by Google

"It is suggested that you install apparatus for the disinfection, by hypochlorites of lime, of the entire waste output of your tannery. That the sedimentation tank be enlarged in order that there may be a period of four hours' sedimentation before the introduction of the chemical solution to the tannery waste is effected and so that four hours of contact may always be secured after the chemical solution has been added.

"That duplicate sewer connections be made to the pump well in order to obviate any discharge of tannery waste into the stream; that the flow from the works to the sedimentation tanks should be regulated so as to render the delivery into the sedimentation tanks more uniform.

"That a roughing filter with facilities for cleaning should be installed at the outlet of the tanks to intercept suspended matters not settled out of the sewage. The type hereinbefore mentioned might be used to advantage. A sand filter of mechanical type should be established as a finishing process. This secondary filter should be provided with facilities for cleaning and the wash water should be collected and evaporated on not less than 60 pounds pressure. And, finally, the sludge from the treatment works should be collected and treated in the centrifugal dryer and be destroyed by fire."

In England the question of tannery sewage has, perhaps, been gone more thoroughly into than elsewhere, possibly on account of the dense population, and there the general method is about as follows: A series of precipitation tanks followed by filter beds made up of coke, coal, cinders or other cheap media, followed by a series of catch tanks, then to sewer or stream. In some plants the settled sewage is run over these filter beds till a bed becomes clogged, then this bed is cut out and allowed to stand for a time to become dry, when it is cleaned of surface accumulation, redressed with additional media and placed in service again. In our own experimental bed we found that the time of service was about three to four weeks, when by removing three or four inches of the surface and redressing, the bed would be effective again for about the same period.

Another method sometimes used where conditions are favorable is to plow a field into wide furrows and allow the sewage

Digitized by Google

to run into these furrows and slowly seep the liquids away while the solid matters remain. After a time the first field is put under cultivation and a second put into commission.

The following extracts from a report on the sewage disposal system at Litchfield, England, should prove of interest, as it is understood this system follows closely the general method for the treatment of tannery sewage in that country.

"The treatment of Litchfield sewage is one of difficulty because of the large amount of trade waste discharged. The system is of the continuous flow type. There are two sets of precipitation tanks of a combined capacity of 244,650 gallons. There are a total of twelve filters of a superficial area of 4,712 square yards, and a cubical content of 7,460 cubic yards. The depth of the filters varies from four feet to five and one-half feet. In other words, the twelve filter beds are about 60 x 60 feet and about five feet deep.

"The medium of the filters, with one exception, is coal and made up as follows: One foot in depth with coal 2 inch to 1 inch in size, and the balance with coal ½ inch to ¼ inch in size. One filter bed was made up with slag in March, 1908, as follows: Six inches deep with slag 2 inch to 1 inch in size, and three feet three inches with ¼ inch to ⅛ inch in size. This filter has been worked ever since and at present shows no signs of deterioration or pooling. The top nine inches of the coal filter beds is being gradually replaced with slag, as it is found that coal is inclined to disintegrate when exposed on the surface.

"The system of distribution of sewage is by means of fixed sprays. About 72 tons each of aluminoferric and milk of lime are used per annum as precipitants. The effluent is generally of good quality, but inclined to deteriorate when mixed with the brook water, with the result that a considerable quantity of flocculent matter and sewage fungus collects in the brook. The dry weather flow of sewage is at the rate of 400,000 gallons for 24 hours, or 45 gallons per head of population. Most of the solid matter is removed in passing through the precipitation tanks. The precipitants (alum and lime) are added after the sewage has passed through the precipitation tanks, and consequently very much better results are secured than when pre-

Digitized by Google

cipitants are added to the raw sewage, besides saving about 75 per cent. of the precipitants. In summer the sewage has about 6¼ hours, and in winter about 10 hours in passing through the precipitation tanks."

In concluding, it might be well to remark that probably no system of tannery sewage disposal which shall meet the requirements of and be passed by the state authorities, can be installed without considerable cost and that the operation of the same will prove both expensive and troublesome. It is understood that the English types of disposal systems, which are perhaps the best, give considerable annoyance and present difficulties of operation that requires constant vigilance both from the tanner and the authorities to keep them properly working, so as to deliver an effluent good in character to the streams. It is unfortunate that no general system of tannery sewage disposal has been passed upon by any of the states, so that a tanner is placed in the unfortunate position of being pressed to do something with his sewage, and not knowing what to do or whether it will be acceptable if he makes an attempt to work out the problem.

It would seem a matter of importance that the National Association of Tanners try, in conjunction with the state authorities where tanneries are numerous, to work out a general system of tannery sewage disposal which would be acceptable to the officials, workable, and within the reasonable means of the tanner to install and operate with a minimum of trouble and expense.

QUEBRACHO WOOD AND ITS SUBSTITUTES.[1]

By Clayton D. Mell and Warren D. Brush.

Quebracho, (Quebrachia lorentzii Griseb.), a South American wood, yielding a valuable extract much used in the United States for tanning high-grade leathers, is not the only wood known by that name. Two other and inferior species, Aspidosperma quebracho-blanco Schlecht and Aspidosperma quebracho-colorado Schlecht, are called white quebracho, or "quebracho blanco," and red quebracho, or "quebracho colorado,"

[1] U. S. Department of Agriculture, Forest Service—Circular 202, Henry S. Graves, Forester.

Digitized by Google

respectively. These two, however, belong to an entirely different family (Apocynaceae including the common dogbane or Indian hemp), from the true quebracho, which is a member of the sumac family (Anacardiaceae). The name quebracho is derived from two Portugese words, "quebrar," meaning break, and "hacha," ax, in allusion to the extreme hardness of the wood. At one time nearly every South American wood that quickly dull an ax was called quebracho, but to-day the three woods mentioned are the only ones of commercial importance to which the name is applied. This indiscriminate use of the name quebracho has resulted in much confusion regarding the identity, distribution, and uses of these woods, and the purpose of this circular is to give the uses and distinguishing characteristics of each. Throughout, the true quebracho, will be referred to simply as quebracho, while the two other species will be called white quebracho and red quebracho, respectively.

Quebracho is found in Argentina, Bolivia, Brazil, Paraguay and Uruguay. It is distributed from the Andes eastward for approximately 500 miles, and from near the mouth of the Parana River northward for about 600 miles, thus growing over a territory of 300,000 square miles. A few writers claim that the Province of Santiago, Chile, once yielded quebracho, but nothing definite exists to show that it ever extended that far westward. Its commercial range is confined chiefly to northern Argentina, in the Provinces of Tucuman, Santiago del Estro and Santa Fe, and the Territories of Formosa and the Chaco and to the Chaco of Paraguay. It is comparatively rare in Bolivia and Uruguay, and in the Provinces of Salta and Jujuy, Argentina.

At the present rate of consumption, the supply of quebracho appears to be practically inexhaustible. Owners of quebracho timber claim that an average acre yields approximately 2 tons of the wood. A very conservative estimate of the total possible yield from the areas where quebracho occurs in commercial quantity places it at 168,000,000 tons, while the present yearly consumption of the wood for all purposes is a little less than 1,000,000 tons. The consumption, however, because of the scattering way in which quebracho grows, entails the cutting over each year of about 500,000 acres.

Digitized by Google

The price of quebracho lands varies greatly. In Paraguay they bring, as a rule, from $6,000 to $7,000 per square league (approximately 4,633 acres), or about $1.50 per acre, though some areas can be purchased for as little as from 15 to 25 cents per acre. In the Argentine Chaco, on the other hand, certain tracts near railroads or waterways sell for $2 per acre or more.

Quebracho never grows in pure stands, but is scattered through open forests composed of many species. Seldom, in fact, are more than four or five quebracho trees found on an acre. It usually attains a height of from 50 to 70 feet, and a diameter of from 2 to 4 feet. It is neither a mountain nor a river-bottom tree, but grows best in the somewhat elevated stretches between the water courses, or in other situations with sandy soil and moderate atmospheric and abundant soil moisture. Its growth during early life is very rapid, fence posts being obtained in ten years, but in later life is very slow. Little is known, however, concerning its average rate of growth to maturity. So far it has been free from attack by insects.

The heartwood of quebracho is one of the hardest, heaviest, and in the region of its occurrence, most durable woods known. Highly tempered tools are required to work even the young green wood, and old wood is almost as hard as metal. It weighs about 78 pounds per cubic foot, and has a specific gravity of from 1.2 to 1.4, sinking, of course, in water. Nine quebracho ties of the size used in Argentina weigh a ton. Its lasting qualities are such that, in Argentina, ties of the wood appear to remain indefinitely in a perfect state of preservation. Logs left in the woods have been found absolutely sound after twenty-five years. The wood contains a very large amount of tannin, which acts as a preservative, and to which its extraordinary durability has been ascribed.

The sapwood of quebracho, forming about one-third of the whole, is nearly white. The heartwood, when freshly cut, is dark cherry-red, but becomes much darker with age. It is fine-grained and takes a beautiful polish.

Quebracho wood is one of the principal commercial products of South America. Though its qualities fit it for use in many ways, its value for tanning extract and crossties is so great that

Digitized by Google

nearly the entire annual cut is put to one or the other of these uses. In Argentina, however, where it is commercially most important, quebracho is employed for more purposes, though not in greater quantity, than any other wood.

There, because it is proof against decay, it finds place in wharves, dry docks, and quays, and as fence posts, beams and cross arms. It is also used for bridge and ship building, general construction, furniture, and interior finish. The timber is usually seasoned for from two to four years before being used.

Quebracho has been adopted throughout its range as a standard crosstie timber and is gradually replacing the cast iron ties once common. In Argentina quebracho ties for broad-gauge roads are nine feet long, ten inches wide and three inches thick, and sell for him $2.00 to $2.50 each. The wood is so hard that spikes can not be driven into it, and holes must be bored clear through a tie for bolts to fasten the rails. About eighteen quebracho ties are got from the average acre, a yield which appears small when contrasted with the forty to sixty first-class white oak or pine ties obtained from an acre of our native forest. The difference is compensated, however, when it is remembered that the life of a quebracho tie may be practically indefinite, while that of our best native ties is seldom greater than eight years. Practically all the quebracho cut for ties is used in South America. Quebracho ties have been tried experimentally in the United States, but were found to lack resiliency and to crack badly with frost. The expense of boring holes for bolts was also another item against them.

The heartwood of quebracho yields from 20 to 24 per cent. of tannin, the sapwood from 3 to 4 per cent. and the bark from 6 to 8 per cent. It is this remarkable production, varying in different parts of the tree's range, which justifies the extensive use for tan extract of a wood so valuable for other purposes. The bark and sapwood are seldom utilized, a fact which seems to indicate unnecessary wastefulness, since the tannin content of the former is equal to that of the lower grades of our native tanbarks; while the content of the latter is but slightly below that of our native chestnut wood.

Besides tannin, quebracho wood contains considerable, though

Digitized by Google

relatively small quantities of red, gambier-like coloring matter used as a filler. Quebracho extract does not contain enough of the non-tannin materials to produce by itself well-nourished leathers, and is therefore mixed in the proportion of 1 to 4, by weight, with other tannin material, such as the extracts of mangrove and chestnut, which are stronger in non-tannin substances.

When cut for tan extract the trees are cleaned of their bark, sapwood, and branches, and then brought to the factory, where they are reduced to shavings or small chips. These are boiled or steamed to release the tannin, and the resulting fluid extract is evaporated to a thick paste, which, when dry, goes to the market in sacks or barrels. The cost of cutting quebracho logs and bringing them to the factory is much greater than that of manufacturing the extract itself. At present logs are hauled chiefly by ox teams to the nearest railroad or boat landing and from there shipped to the extract plant. It is in Paraguay, where quebracho trees are very scattered, that the transportation of logs is most difficult and expensive. Little or no market exists for quebracho timber or extract there, and practically all of the wood is shipped to Buenos Ayres, where it is either consumed for extract or exported.

Quebracho obtained from the Provinces of Santiago del Estero and Santa Fe, Argentina, is particularly rich in tannin, and there also the trees reach their largest size. It is chiefly in these Provinces that quebracho is being extensively lumbered, the output steadily increasing from year to year. In the Provinces of Salta and Jujuy, where quebracho is rare, the inhabitants prefer for tannin the bark of two trees, Acacia cebil Griseb, and Pipta denia cebil Griseb., locally known as cebil. These barks are exceedingly rich in tannin material, in the case of the latter, at least containing from 19 to 25 per cent.

Quebracho wood and extract are now the leading exports of Argentina and Paraguay. Since their introduction in 1888, imports of these into the United States have increased steadily. In 1910, 38 per cent. of all the tannin material used in the United States was quebracho. Nearly all of this came from Argentina. Table 1 shows the quantity and value of material imported during the fiscal years 1907 to 1910, inclusive.

Digitized by Google

WOOD.

Year	Tons	Value
1907	66,810	$ 840,779
1908	48,871	612,971
1909	66,113	731,795
1910	80,210	1,058,647

EXTRACT.

Year	Pounds	Value
1907	76,033,584	$2,319,785
1908	79,186,787	2,260,364
1909	102,004,981	2,740,530
1910	95,183,073	3,021,902

Quebracho wood enters the United States free of duty. A duty of from one-half to three-fourths of a cent per pound, however, is levied on the extract, which, in the new (1909) tariff schedule, is divided into two classes, according to its density or the percentage of tannin it contains. If less in density than 28 degrees Baumé the duty is one-half cent; if greater it is three-fourths of a cent. Transportation from Argentina to the United States is so cheap that many importers bring in logs and extract the tannin in this country, thus saving the high import duty. The price of quebracho extract f. o. b. Montevideo or Buenos Ayres, the two principal exporting points, is from $80 to $85 per ton, and that of logs from $14 to $20 per ton.

SUBSTITUTES FOR QUEBRACHO.

Both of the other woods which go to the market as quebracho, the white and the red, yield a relatively low percentage of tannin, and it is therefore unlikely that they are knowingly substituted to any extent for the true quebracho. Often, however, they may unintentionally be substituted for quebracho, through similarity of names. Quebracho is frequently called quebracho colorado, and red quebracho is also called this, and often merely quebracho. White quebracho, too, goes under the latter name. While quebracho and red quebracho may resemble each other superficially, white quebracho is readily distinguished from either by its light color. White quebracho is commercially more important than the red, and in some parts of South America has been used as a substitute for quebracho. It yields a much lower percentage of tannin, but the tannin itself is not essentially different from that of quebracho.

Digitized by Google

White quebracho is common throughout the regions where quebracho grows. It is most abundant in the wetter parts of northern Argentina, in the Provinces of Cordova, Santa Fe, Catamarce, Santiago del Estero, the southern portion of Tucuman, and the Chaco. It is an evergreen tree, reaching a height of from 60 to 100 feet, a diameter of from 1 to 3 feet, and is remarkable for its erect stem and wide spreading crown. It is usually less bulky than quebracho, and branches nearer the ground, features which help to distinguish it in the forest.

The wood is strong, hard, and very heavy (specific gravity from 0.88 to 1.1), very close-grained, yellowish white in color, with a pinkish or rosy tint. It is not very durable in contact with the soil, yet much in demand for fence posts, rafters, flooring, railroad trucks, crossties, cabinet work, turnery, hubs, spokes and cogwheels. Its dense, uniform structure makes it suitable as a substitute for boxwood (Buxus sempervirens L.) in wood engraving. Unless very carefully seasoned, however, it is likely to warp and twist, and is said to be subject to insect attack.

Red quebracho is also abundant throughout quebracho's range. Its wood when freshly cut is red, but becomes dark brown with age. It is used for practically the same purposes as white quebracho. Although in general its structural characters are similar to those of the former, it is said to be more durable in contact with the soil. While red quebracho may at first sight be mistaken for quebracho, its structural characters distinguish it. Moreover, its commercial importance is relatively so small that it is seldom mixed with the other wood.

(The circular closes with descriptions of the characteristics of the three woods as seen under the microscope, by means of which they may be distinguished.)

REPORT OF THE INTERNATIONAL COMMISSION ON PRESERVATION, CURE AND DISINFECTION OF HIDES AND SKINS.

Condensed from *Collegium* Supplement, June, 1912.

This Commission was appointed by the Brussels Conference, 1908, Alfred Seymour-Jones being Chairman. There were 41 members from 10 countries. The Commission proposed to col-

Digitized by Google

lect information as to the various methods of preservation, cure and disinfection employed all over the world, to investigate the methods authorized or recommended for disinfection, and to devise or recommend a method or methods for preservation, cure and disinfection of hides and skins. A list of 39 papers bearing on the subject is given. They include papers on the methods employed in England, France, Germany, Italy, Hungary, Japan, West Africa, New Zealand, India, East India, and Australia. Ten of the papers on other topics have appeared whole or in abstract in this Journal.

It was the original intention to confine the work of the Commission to the methods used in handling the flayed hide, but they have found it necessary to include a study of injuries to the hide of the living animal, and those due to improper flaying. A conference was held July 29, 1909 at which representatives of the various trade organizations interested in the subject were present. An Allied Trades Committee was organized, which has been working in connection with the British Board of Agriculture. Leaflets have been issued on the warble fly, anthrax, and many other topics. *The Syndicat General des Cuir et des Peaux de France* has formed an association for the destruction of the warble fly. This association has collected and published the literature of the subject. The Belgium Leather Bourse has published much information in regard to improved methods of flaying.

The conditions of hides and skins as offered for sale are classified as follows; (1) Unsalted, wet and fresh from slaughter house, (2) lightly salted, (3) heavily salted, (4) salt brine, (5) sodium sulphate cured, (6) pickled, with acid and salt, (7) dry salted, (8) earth cured (paste), (9) flint or sun dried, (10) air dried. In Great Britain many hides are sent from the slaughter houses to the tanneries without being cured at all, and in some instances tanners pay to have the hides salted before shipment. On the continent public slaughtering is in general compulsory, but not in England, where private slaughtering is the rule. The method of flaying with a hammer is gaining favor on the continent. The hide is caught in a basket, in which it is allowed to cool before salting. It is then opened out, in some

Digitized by Google

instances cleansed from blood and dirt, and receives 25 per cent. of its weight of salt. The next hide is laid on top and also salted, and so on until a convenient pile is made. Most other countries follow the continental method of salting.

Anhydrous sodium sulphate is being largely used as a substitute for salt. It does not run away like brine, but remains in the hide, which swells well in the limes and liquors, which chlorides have a tendency to prevent. Ten to fifteen per cent. of the weight of the hide suffices. Some tanners object to this method because it alters the white weight of the hide.

Pickling with an inorganic acid and salt is but little used for hides, but is much used for sheep and goat skins. It is a cheap method, and serves where oversea transportation or long storage is necessary.

The committee of the Royal Society of Arts on Bookbindings condemned the method as producing unsound leathers. In many cases moulds form, which injure the skins. The substitution of formic acid for the mineral acid presents marked advantages. Skins pickled with formic acid and salt were sent to various parts of the world and returned, to test the process. In all cases they arrived in sound condition. Formic acid prevents the growth of mould. It forms no stable compound with the hide and so may be washed out.

Earth cures are peculiar to certain northern districts of India, in Bengal and the Punjab. The paste, which is a local natural product, is neutral to litmus. It contains sodium sulphate, some magnesium sulphate and common salt, mixed with earthy matter containing calcium carbonate. In the Bombay Presidency common salt is generally used. The method of curing, both with salt and with earth paste is to spread the hides on the ground, flesh up, rub on the cure, work it in with a brick, and then expose the hide in the sun to dry. Sometimes the hides are sprayed with a solution of arsenic and caustic soda as an insecticide. In some districts wood ashes is used with salt. Many hides are spoiled in drying, receiving "sun-blisters" and other injuries.

Methods involving drying without salt are used where salt is

Digitized by Google

difficult to get and where transportation is expensive. Many methods are used. The hide may be laid on the ground in the sun, flesh side up, or stretched in a frame and dried either in the sun or shade. Sometimes the hides are hung up by the flanks, and sometimes hung over poles, either side out, and dried in the sun or in the shade. When dried in the sun, the surface drying first forms a horny covering through which moisture escapes slowly, and the interior is often injured by being overheated while moist. Thus "blisters" are caused, which do not appear until the hide is soaked. Insects also cause much trouble. It is difficult to detect defects in dried hides. One method used in India involves leaving much flesh adhering, then slashing this with a knife to promote drying. The cuts often penetrate to the hide, causing serious injury which does not show until the hide is fleshed in the tannery. Dried hides and skins have often been known to convey disease, most frequently anthrax.

In Japan the hides are first washed, then spread flesh side up on a low platform. On each hide is spread from 7 to 10 pounds of salt, and they are thus piled to a depth of 4 feet, being left in pile for three days before shipment to the tannery. If they must be kept longer, a second salting is given, 10 to 12 pounds of salt per hide being used. Korean hides are usually sun-dried.

The Commission recommend that hides be cured by piling with salt or sodium sulphate, after being washed. Drying is condemned, as also pickling with mineral acids and all forms of earth cures. The use of salt which has been used and swept or shaken off from other hides, is condemned. For denaturing salt, 10 per cent. sodium sulphate, 1 per cent. naphthaline and one-60th of one per cent. bichromate of potash is recommended.

No instance of the conveying of disease by wet-salted hides has been confirmed, but it has been suspected that foot-and-mouth disease was so conveyed. The conveyance of anthrax by dry hides has been abundantly proved. Three methods of disinfection were put forward by the United States Government a few years ago; (1) immersion in a one-tenth per cent. bi-

Digitized by Google

chloride of mercury solution for one-half hour; (2) immersion in 5 per cent. carbolic acid for one-half hour: (3) by exposure to SO_2 for six hours in a closed room, hides hung separately, four pounds of sulphur being burned per 1,000 cubic feet of room capacity. None of these methods is satisfactory. Neither 5 per cent. carbolic acid nor SO_2 kills anthrax spores, and mercuric chloride is precipitated in the presence of hide substance and so rendered ineffective. J. H. Yocum has suggested the use of mercuric chloride in a saturated solution of common salt as a means of sterilization. (See this Journal, Vol. V, pp. 507-10). This conbination originally suggested by Blumberg and later employed by Von Esmarch, Kuebler and Lafar to prevent the formation of albuminates in the presence of mercuric chloride, is effective in sterilizing anthrax spores in from 3 to 8 hours when one per cent of bichloride is present. This percentage is dangerous and inadmissible. Mr. Yocum does not support his claims for this method with definite evidence. The commission recommends that this method be tried, and they believe than one part of bichloride to 5,000 of saturated salt solution should be sufficient. The formic-mercury process of Mr. Alfred Seymour-Jones (See this Journal, Vol. VI, pp. 85-100) has been exhaustively tested, bacteriologically and commercially, and has been found efficient. The dry hides are soaked in a one-half per cent. to 1 per cent. solution of formic acid containing 0.02 per cent. mercury bichloride for 24 hours, and then placed in brine. The acid prevents the formation of insoluble albuminates, and no injury to the hides results. The commission recommend that the process be applied to dry hides at the port of shipment, and that the hides be then shipped in the wet-salted condition. The cost is not more than 7½ cents per hide. The process has been tested by Dr. Constant W. Ponder, Prof. Procter, Dr. Stiasny and Dr. J. G. Parker. Parker finds that dry hides soaked with formic acid give a higher yield of leather than those soaked by the ordinary methods. Dr. Becker, of Frankfurt, has had success in killing anthrax spores with mustard oil. Professors Schattenfroh and Kohnstein of Vienna report success with a 2 per cent HCl, 10 per cent. salt solution at 40 degrees C. In the hands of some other experimenters this

Digitized by Google

method has not been successful, and it is open to the general objection that mineral acids are apt to injure the skins.

Report on Salt Stains. By Dr. Georges Abt.

(The substance of this report is embraced in a fuller report from Dr. Abt given in the following paper).

The last four pages of the report of the Commission are devoted to a summary of the recommendations distributed through the body of the report.

THE ORIGIN OF SALT STAINS.[1]

By Dr. Georges Abt.

Hides which have been cured with salt often show stains, and are thereby depreciated in value. Although these stains are all attributed to the salting, they are probably of various origin as well as various in appearance. I have been led to this unexpected conclusion in studying a group of these stains on calfskins from four sources. In the skin with the hair on, there appear on the flesh side small rust colored spots, with the consistency of a damp crust. After unhairing, they show on the grain, where they form slightly raised designs of festoon shapes, slightly yellow in color, and during tannage the color becomes gray-black or dark brown.

In an important hide-warehouse these stains appeared with regularity, despite all the minute care taken in salting. Two years elapsed, and at the exact time when salt from a new source was procured, the stains disappeared or became so rare as to be unnoticed. The analysis of the new salt differed from the old in one point. The latter contained about 4 per cent. of calcium sulphate, mainly in the form of concretions known to the salt trade as grains of "schlott" comprising one molecule of calcium sulphate to one of sodium sulphate. Examining a pile of stained skins, I have found many of these grains, adhering to

[1] *La Halle aux Cuirs*, July 28, 1912.

Digitized by Google

the spots. They are often sunk in small depressions, surrounded by a little brown material and stuck to the hide. These grains, taken from the spots, contain 21 per cent. of organic matter, traces of iron, and phosphoric acid, (about 4 per cent P_2O_5).

The analysis of the surface layers of the skins themselves gave the following figures for 100 parts of dry matter.

INSOLUBLE PART.

	SO_3	P_2O_5	Ca
Stains	2.27	6.83	6.15
Parts not stained	0.95	0.35	0.57

SOLUBLE PART.

Stains	0.86	0.34	0.45
Part not stained	0 65	0.18	0.19

Skins tanned with sumac, and stained on the the grain, from an entirely different source contained as follows:—

	SO_3[1]	P_2O_5	Ca
A—			
Stained	0.67	0.360	0.63
Not stained	0.99	0.007	0.21
B—			
Stained	0.60	0.270	0.47
Not stained	0.66	0.022	0.20
C—			
Stained	not det.	0 320	0.47
Not stained	not det.	0.057	0.19

The stains were always exceptionally rich in phosphoric acid and in calcium while the whole skin, tanned or untanned, contained an abnormal amount of sulphuric acid. This phosphoric acid can hardly be assigned to any other origin than the nucleic acid of the nuclei of the epidermal cells and hair follicles. The skin with the hair on contains from 0.45 to 0.56 per cent. of P_2O_5 in this form. But, by autolysis or the action of micro-organisms, this phosphoric acid is detached from its organic combination and passes into the state of a soluble phosphate, phosphate of ammonia no doubt. I have found in skin almost fresh 36.7 per cent. of the phosphorus present to be in the soluble state, against 78.5 per cent. in an overheated skin and 66 per cent. in a skin preserved in salt. Under normal conditions the skins are relieved of the soluble phosphates in the soaks,

[1] With a deduction of 0.2 per cent., representing approximately the sulphur normal to the hide.

Digitized by Google

and the organic phosphates are removed with other organic material in the process of preparation for tannage. But if the salt contains calcium sulphate, this reacts with the ammonium phosphate to produce insoluble calcium phosphate. The sulphate of ammonia formed diffuses itself through the skin. Its presence may be directly determined, proving that this reaction actually takes place. If a large piece of skin, partially stained, be divided and one part ashed alone and the other with addition of sodium carbonate, and the SO_3 determined in the ash, a difference of 21.7 per cent. in the amounts is shown, due to the volatilization of a part of the SO_3 in the former case.

Sometimes on skins tanned with chrome, (one bath), many small green salt stains appear on the flesh side. On treating tricalcium phosphate in slight excess with basic chromium chloride, I have obtained the complete precipitation of the chrome, half as phosphate and half as oxide, the color of the precipitate being exactly that of the spots.

There is such a concordance among these facts that the influence of calcium sulphate or phosphate on the formation of the stains cannot be denied. It is confirmed by experiments which I have made to reproduce these stains. Among many trials, only those have succeeded in which I have provoked the precipitation of calcium phosphate on one side or the other of the skin.

It is, however, difficult to imagine by what reactions phosphate of calcium, a salt in itself colorless, and which would not appear capable of energetic action on the skin, determines the appearance of the stains. They are without doubt the product of complex phenomena in which are concerned traces of salts of iron, (which are always present in the stains), and also bacterial processes, but I have not yet clearly and precisely defined the role of these two factors.

There are certainly two kinds of salt stains and perhaps more. What precedes concerns only one kind. These stains, besides calcium phosphate contain traces of salts of iron. But if one studies the question further he is led to a contradiction. The stained tissues always give the reaction for iron with greater intensity than the neighboring unstained tissues, but if the

Digitized by Google

quantity of iron in the two parts be determined, it is found practically the same. This proportion is very small. Of the whole thickness, the proportion is abount 0.01 per cent. while the superficial layer on the flesh side has ten times as much. These quantities are greater than those carried by salt, sea salt and rock salt being practically identical. The excess is perhaps due to accidental contacts and to blood.

The problem is therefore as follows: How does the same quantity of iron produce stains in one place and not in another? The iron exists on the surface of the skin in an *insoluble* condition. It stains when it has been carried into solution, which diffuses over a limited range, and is again precipitated in small colored spots. Stains of the same color and extent, may be produced with equivalent quantities of very small crystals of iron alum, or iron chloride. How does the solubilization come about? The only hypothesis which explains the localization in the neighborhood of the grains of calcium sulphate is that the iron, in the state of insoluble ferrous carbonate, is dissolved by the ammonium sulphate, the formation of which in the neighborhood of these grains has been demonstrated. The study of the solubility of ferrous carbonate in solutions of ammonium sulphate has proved that the concentration of the sulphate of ammonia is not sufficient except on the surface of the stains. But one cannot produce a stain by using traces of ferrous carbonate and crystals of ammonium sulphate. The iron seems to be too widely scattered, perhaps because the quantity of ammonium sulphate added is too great. This lack of success is the only objection to the hypothesis which has been stated. It is one of the reasons why the coöperation of bacteria in the production of the stains seems probable.

The best argument in favor of bacterial action is that the reactions by which chemical agents alone can produce great changes in the skin remain very obscure. It is necessary to add that the intervention of bacteria is not much more easy to comprehend. It has been remarked that the stains occur chiefly in summer, that they appear after some time, and that they demand a certain degree of dampness in the skin. The same conditions would favor certain chemical reactions.

Digitized by Google

In every case, cuts made in the stained skin and leather show (1) that the bacteria have not penetrated to the interior of the tissues, (2) that even when the grain is much altered, the superficial hyaline layer remains intact. Bacteria have been isolated from six groups of stains. The species are generally the same as those found on sound hides. It has been impossible to see how the precipitation of calcium phosphate can have any connection with these bacteria.

Many species are capable of energetic action on hide. But which of the products of this action contribute to the stains? Perhaps ammonia, in precipitating the soluble salts of iron, perhaps carbon dioxide, which may contribute to the solubilization of the iron. Perhaps the colored products are derived from phenolic substances, the latter being derived from chemical change in the hide. The participation of no one of these agents in the formation of the stains has been shown with the same certainty as the role of sulphate of lime.

All these results are confirmed by the experimental reproduction of stains which has been realized in three series of experiments: first, on the flesh side of skin with the hair on, by depositing grains of sulphate of calcium and crystals of phosphate of ammonia; second, on the hair side of the skin with drops of solution of phosphate of ammonia and calcium chloride; third, on the grain of unhaired skin with phosphate of ammonia in solution and either powdered sulphate of lime or a solution of calcium chloride. The addition of traces of ferrous carbonate favored the production of stains, principally on the grain, and influenced the color. All these stains behaved like natural stains throughout all the tanning processes.

As to the second type of stains, they extend less deeply into the thickness of the hide, otherwise they are only visible on the grain. This is perfectly smooth without swelling or folding. These stains do not contain phosphate of lime but are about 30 per cent. richer in iron that the nearby parts. Perhaps they are merely due to the formation of soluble ferrous bicarbonate in consequence of microbic fermentation. But the matter has not been sufficiently studied to establish very firmly this hypothesis.

Digitized by Google

What is the relative frequence of these two sorts of stains? The first have been met with on calf skins from four different sources; the second only on horse-hides at one tannery. Analysis of the skins would easily show whether the stains belonged to one class or the other.

It would seem that rock salt contains sulphate of calcium more often, at least in the form of grains, than sea salt. However, rock salts have been examined which were exempt from it, and sea salt also contains a little sulphate of calcium. It is enough that it be gathered into small spots to form stains. Finally it is necessary, in order that a salt containing calcium sulphate may produce stains that the different conditions be brought together. Some of these conditions have been brought to light, perhaps not all. With regard to stains of the second type, it appears useful to clean the blood off the skins, to salt sufficiently, to avoid an excess of dampness. Experiments should also be made on the addition of weak antiseptic salts.

ABSTRACTS.

Meeting of the German Section, I. A. L. T. C., June 16, 1912, at Frankfurt. *Collegium*, 507, pp. 258-266. The new form of *Collegium* was discussed, and it was suggested that articles in it be printed in all three languages. The Editor replied that the cost would be prohibitive. He promised, however, to make an index at the end of the year giving titles of papers in all three languages. Dr. Paessler reported on *Sugar Content of Tanning Materials and Extracts.* He remarked that Von Schroeder's method estimates the various grape-sugars, not materials like cane-sugar. It is important to be able to estimate these, not only because they contribute to the formation of acid in the liquors, but because their presence may indicate adulteration of extracts with molasses. Oak bark, valonia and myrobalans contain no cane-sugar-like materials. Pine and spruce bark have more than others. The speaker said that the proportion of tannin to non-tans in an extract, and also the proportion of grape-sugar-like substances to those of the cane sugar class depend not only on the nature of the raw material but on the method of extraction. This is especially true of chestnut extracts. High pressure and temperature during extraction tend to raise the non-tan and sugar content of the extract. Experiments with mallet-bark extracts showed that leather tanned with extract having high non-tan content was darker, and somewhat woody in texture.

Digitized by Google

The Adulteration of Tanning Extracts with Sulphite-Cellulose Extract was discussed by Dr. Paessler. In his experience, cellulose extract alone does not produce in general a usable leather. Various hides and skins were tried, and only in one instance, where the tannage was continued for more than a year, was the result like leather in character. This leather was, however, soft and flabby and gave a very low yield, lower than sulphited quebracho under similar conditions. It is difficult to tell, in the case of mixtures of cellulose with other vegetable extracts whether the tanning effect is wholly due to the other material or whether the cellulose helps. Exact researches are being carried out at the Freiberg Institute to test the Procter and Hirst anilin and HCl reaction for the detection of sulphite-cellulose extract. It has been shown that in order to obtain dependable results it is necessary to follow accurately the directions given by Procter and Hirst (see this J., Vol. IV, p. 147) in regard to the proportion of anilin and HCl. In the absence of cellulose extract, the reaction gives negative results, even when quebracho wood was extracted 12 hours at 2 atmospheres pressure without bisulphite, or 5 hours at the same pressure with 4 per cent. bisulphite. The reaction takes place when the extraction is carried out with the bisulphite at 6 atmospheres, but this condition is never realized in practice. Careful use of this method suffices therefore to detect cellulose adulteration. Experiments showed that anilin hydrochloride could not be used instead of anilin and free hydrochloric acid, a precipitate forming in the absence of sulphite-cellulose extract. The speaker remarked that small percentages of sulphite-cellulose are very deceptive. Dr. Becker objected to the word adulteration as applied to mixtures of tanning extracts with sulphite-cellulose, since such mixtures are useful and legitimate. Dr. Parker remarked that when extracts are made from dead or decayed wood, they may give the Procter-Hirst reaction in the absence of sulphite-cellulose. Several speakers cited instances of good leather made with mixtures containing sulphite-cellulose extract.

Mr. Kallab described his apparatus for testing the effect of light on dyed and natural leathers. Sunlight is concentrated on the sample by a lens, which is moved by clockwork so as to keep the light on the same spot for several hours.

The Analysis of Sulphonated Oils as Used in the Tannery. U. J. THUAU. *Collegium*, 507, pp. 280-4. Paper read before the French Section, I. A. L. T. C., May 25, 1912. Oils which have been treated to a greater or less extent with sulphuric acid are generally called sulphonated or sulphated oils. These include neats-foot, olive, castor, and some other saponifiable oils. They are finding a rapidly increasing use in connection with both chrome and vegetable tannage. When sole leather is made by tanning partly in vats and finishing in a drum, there is a great advantage in adding to the liquor in the drum some mineral oil to which has been added sulphoricinate of soda (sulphonated castor oil). The

Digitized by Google

sulphonated oil dissolves in water, and this solution mixes in all proportions with mineral oil. In the presence of the sulphonated oil, the mineral oil is able to penetrate the leather to a small extent, and without diminishing its firmness enables it to retain a certain amount of moisture in the interior and so prevents cracking. Certain very hygroscopic mineral salts have this effect also, but they load the leather undesirably. Another purpose is served by the presence of the mineral oil and sulphonated oil. It facilitates the penetration of the tannin, and also by oiling the outside of the leather, diminishes the friction against the drum. To 200 gallons of liquor at from 10° to 15° Bé, 40 pounds of mineral oil and one pound sulphonated castor oil (50 per cent. water) may be added.

The retannage of sole leather in a drum with special decolorized extracts is now much practiced. In this work, some sulphonated castor oil is put into the wheel either at the beginning or a half hour before the close of the process. The soluble oil penetrates the leather and serves two purposes. It prevents the grain from cracking (which is always to be feared when the rendement is pushed very high), and bleaches the surface of the leather. It also prevents the uncombined tannin in the leather from oxidizing in the process of drying. Sulphonated oil may also be used to advantage after rolling, a very light coat (50 per cent. water) being brushed over the grain before hanging up to dry. Sometimes a mixture of equal parts light colored mineral oil and 50 per cent. solution of sulphonated oil is used in this manner.

The tannage of upper leathers may be finished in the drum; 40 pounds fish oil emulsified with 2 pounds sulphontaed castor oil is added to 100 gallons of liquor of 10° to 50° Bé, which is often half quebracho and half chestnut. Leather so tanned has a very pleasing soft "feel." Good results are obtained by stuffing small tanned skins, such as sheep, with a mixture of refined mineral oil and sulphonated castor or neats-foot oil. A good mixture is: 50 pounds sulphonated neats-foot oil, 50 pounds water and 25 pounds mineral oil.

Sulphonated oils are extensively used in fat-liquoring chrome leathers. They have a serious disadvantage in the case of leather to be used in combination with rubber, for while the leather will stand the temperature necessary to vulcanize the rubber, sulphonated oils are liable to be decomposed at this temperature (150° C., 300° F.). For use with chrome leathers, any animal oil capable of furnishing with sulphuric acid oxy-stearic-sulphuric acids is suitable. Neats-foot oil is particularly satisfactory. It should be sulphonated completely, so that after neutralization it is almost solid, and will keep for months. Five or six pounds of this thick material are enough for 100 pounds of leather. This is dissolved like soap in boiling water, or better in an emulsifying apparatus. It should be drummed into the leather at a temperature from 55° to 60° C. (130°-140° F.). This fills the leather well and does not spew.

Good results are obtained by mixing sulphonated neats-foot and castor

Digitized by Google

oils with other oils, either before or after sulphonation. According to some writers, sulphonated castor oil, or sulphoricinate of soda, is a sulphuric acid ether of a non-saturated fatty acid. This may explain the fact that it is capable of fixing much oxygen, and in consequence of this action prevents oxidation of tannin on the surface of the leather. To sulphonate castor oil, a very thin stream of sulphuric acid (66° Bé) is poured into the cold oil, which is kept in motion by a mechanical stirrer. An excess of acid must be used; about 20 per cent. as much total acid as oil is a good proportion. The temperature rises a little and there is a slight liberation of SO_2. After some hours, cold water[1] is added, and afterward the aqueous layer is drawn off. Repetition of this process removes most of the excess of acid. The residue may be neutralized by ammonia or soda, producing sulpho-ricinate of ammonia or soda. The process for sulphonation of neats-foot oil is essentially the same, except that in preparing the thick product for fat-liquoring chrome leather the temperature should be above 60° C. (140° F.) both during sulphonation and neutralization.

Analysis of Sulphonated Oils.—The most important point is the proportion of sulphated fatty acids. Five to ten grams of the sulphonated oil are placed in a long flask of thick glass, capable of being hermetically sealed so as to withstand heavy pressure. Twenty-five cc. pure HCl and 25 cc. water are added. The flask is now heated to 140° or 150° C. (284°-302° F.), either in an air-oven or on an oil-bath. After an hour the flask is taken out and allowed to cool. About 50 cc. of water are added. The whole is then filtered, the fatty acids remaining on the filter. The sulphuric acid is determined in the filtrate by the customary method with $BaCl_2$. The molecular weights of oxy-stearic-sulphuric acid and ricinic-sulphuric acid being 380 and 378 respectively, that is to say, nearly equal, it will suffice in order to find the proportion of sulphuric fatty acid, to multiply the figures for sulphuric acid found, and the per cent. of oil, by 4.738. In sulpho-ricinate of soda, (50 per cent. water), this content of sulphuric fatty acids varies between 15 and 20 per cent. If there is free sulphuric acid, it must be titrated separately and deducted from the total determined as above. To determine this free sulphuric acid, the sulphonated oil is treated with soda, ashed, and the Na_2SO_4 determined in the ash. To determine the total fatty matter, weigh 4 gr. sulphonated oil into a tared dish, dilute with 20 cc. water, and if the liquid is cloudy, add phenolphthalein and clear by adding ammonia to feeble alkaline reaction. Dilute 15 cc. of H_2SO_4 with an equal volume of water and add, also 6-8 gr. stearic acid, and boil until clear. Cool. Detach the cake composed of fatty matter and stearic acid; dry and weigh it. Deduct the stearic acid added, to find the total fatty matter. In reporting results, it must not be forgotten that the sulphuric fatty acids are a part of the total fatty matter. A sample

[1] The author does not mention the addition of salt with this added water, which in my experience has seemed necessary to prevent the oil from dissolving in the water.—ED

Digitized by Google

analysis gave: Water and volatile matter (ammonia), 53.6 per cent.; ash, 0.6 per cent.; sulphuric fatty acids, 16.3 per cent.; neutral oil, 29.5 per cent.

Butyric Acid in the Tannery. THEODOR SALOMON, instructor in the Vienna Research Station. *Collegium*, No. 507, pp. 284-7. The property of butyric acid of forming very soluble lime compounds, and the mild action which it exerts on the hide have long recommended it as a deliming agent. Only recently has its price, in consequence of Dr. Effront's process, been reduced to such a point that it may be used economically in the tannery. There have been differences of opinion in regard to its use, some authorities holding that it dissolves a relatively large amount of hide substance, and is therefore not economical. Experiments carried out at the Vienna Research Institute show that this opinion is unfounded. Butyric acid, at the concentrations used in the deliming process and at a temperature under 30° C. (86° F.) works with certainty, neutralizing the lime without bad effect on the grain. Heavy hides in pits require 15 hours, which may be much reduced by the use of drums or paddle wheels. White hide delimed with butyric acid shows a pliant and yet firm texture, may be split thin, and used in the manufacture of articles requiring a close firm grain. Because of its favorable influence on texture and grain, butyric acid is used in pickling hides for chrome tannage.

The principal objection to the use of butyric acid has been a supposed bad influence on quality and rendement due to solvent effect on the hide substance. The acid has but a feeble swelling effect, and the following experiments show that it does not dissolve hide substance to an appreciable extent. Buffalo hides were used, being treated with acid of various concentrations for periods of from 7 to 48 hours.

Concentration of butyric acid per cent.	Time hours	Dissolve nitrogenous substance per cent.
0.5	7	0.07
0.8	7	0.07
1.2	7	0.10
0.5	30	0.075
0.8	30	0.09
1.2	30	0.13
0.5	48	0.10
0.8	48	0.10
1.2	48	0.11

The dissolved material is purposely called nitrogenous substance, and not hide substance. It seems to be due to a compound of lime with albumen, not soluble in water but easily dissolved by acid, formed in the liming process and carried over into the bate adhering to the grain. Even supposing this nitrogenous material to be hide substance, 0.13 per cent. is an insignificant amount.

Digitized by Google

Another series of experiments used deer-hide: 0.5 per cent. butyric acid dissolved in 6 hours from a hide previously delimed with hydrochloric acid 0.09 per cent. nitrogenous material; 0.8 per cent. butyric acid in 30 hours dissolved 0.10 per cent. nitrogenous material from a hide simply washed from the limes; 1.2 per cent. butyric acid dissolved in 48 hours from a hide washed from the limes 0.11 per cent. nitrogenous substance. It is thus shown that the acid behaves similarly toward firm hides and those with loose texture.

In another series, hides were subjected for 6 days to the action of water, butyric acid, hydrochloric acid, formic acid and sulphuric acid. The butyric acid was an 0.8 per cent. solution, and the others of a strength equivalent to that. The quantities of dissolved nitrogenous material were, respectively, 0.45 per cent., 0.20 per cent., 0.18 per cent., 0.36 per cent., 0.60 per cent.

It has been shown that butyric acid acts unfavorably toward the growth of moulds, and so is a partial antiseptic. When the fermentation of the bran bate goes wrong, and butyric acid fermentation replaces the usual lactic acid fermentation, the hides are injured. This injury has been charged to the butyric acid, which is quite unjust, as it is due to the fermentation whose final product is butyric acid. No such result is chargeable to ready-prepared butyric acid. L. B.

Tannin. K. FEIST. *Berichte*, **1912**, 45, 1493-5. In connection with the recent work of Fischer and Freudenberg (*J. S. C. I.*, 1912, 503), the author points out that he showed in 1908 that Turkish gall nuts contain a crystalline compound (glucogallic acid), which on hydrolysis yields one molecule each of gallic acid and glucose. The same compound was also isolated from commercial tannins of similar origin. The glucose content of tannin is, however, not due entirely to glucogallic acid, for tannin which has been freed from the latter compound as far as possible by extraction still yields glucose on hydrolysis. In the hydrolysis of tannin the chief quantity of gallic acid is produced readily, but a smaller portion is obtained only with difficulty; possibly glucogallic acid is present in the tannin molecule, together with other molecules of gallic acid in ester-like combination. The failure of Nierenstein (*Chem. Zeit.*, 1909, 126) to obtain glucose on hydrolysis of tannin was probably due to the method employed, glucose being decomposed on boiling with alkaline solutions. The methods of purifying tannin used by Fischer and Freudenberg (*loc. cit.*) would not remove the whole of the glucogallic acid.

A. S. in *J. S. C. I.*

Constitution of Tannin. R. J. MANNING and M. NIERENSTEIN. *Berichte*, **1912**, 45, 1546-51. Fischer and Freudenberg (*Ber.*, 1912, 915-35; *J. S. C. I.*, 1912, 503; this J., 1912, 390) found that carefully purified specimens of Kahlbaum's tannin and of Merck's tannin yielded 7-8 per cent. of glucose on hydrolysis, and concluded that tannin is a pentadigalloyl-glucose. Manning, (*J. Am. Chem. Soc.*, 1910, 1312-190; this J., 1910, 573-81), using a specimen of Schering's tannin purified by Walden's method (*Annalen*,

Digitized by Google

90, 340), prepared therefrom a pentaethyl ester of pentagalloyl glucoside, and concluded that tannin is a pentagalloyl glucoside. The authors now confirm a previous statement of Nierenstein (*Chem. Zeit.*, 1909, 34, 126), that *Tanninum levissimum purissimum* (Schering) yields no glucose on hydrolysis with alkali, and consider that the general glucoside character of tannin is not established. Experiments are described showing the diminution of the optical activity of tannin when its aqueous solution is boiled in a current of hydrogen. This is considered to be due to the transformation of a polydigalloyl-leucodigallic anhydride into the corresponding acid of weaker optical activity. In accord with this view is the fact that a diminution of optical activity is also observed on treating tannin solution with a drop of pyridine, for Nierenstein (*Annalen*, 1912, 388, 252) has shown that polydigalloyl-leucodigallic anhydride is converted into the acid by pyridine. A. S. in *J. S. C. I.*

Chemistry and Analysis of Fats for 1911. W. FAHRION. *Zeit. angew. Chem.*, 1912 [25], 870. *Bibliography.*—J. Marcusson: Laboratoriumsbuch für die Industrie der Oele und Fette. W. Fahrion: Die Chemie der trockenden Oele. Ubbelohde-Goldschmidt: Handbuch der Chemie und Technologie der Oele und Fette, Bd. III, Abth. 2. J. Leimdörfer: Beiträge zur Technologie der Seife auf kolloidchemischer Grundlage. *Analysis.*—The use of trichlorethylene for extraction is established. According to A. E. Outerbridge (*Chem. Revue*, 18, 305), the fluorescence of mineral oils may be intensified by the electric light so that 1 per cent. may be detected in fat oils; debloomed oils also become fluorescent. Meyer and Eckert (*Chem. Zentralbl.*, 1911, I, 742) use lithium hydroxide for saponification; the soap solutions do not gelatinize and filter easily. As an indicator in the saponification of dark fats and residues, J. Marcusson (*Zeit. angew. Chem.* [24], 1297) recommends a mixture of 3 cc. 1 per cent. phenolphthalein, 3 cc. of 3 per cent. alkali blue (alcohol solution). P. Falciola (*Chem. Zentralbl.*, 1911, I, 382) separates solid and liquid fatty acids by saturation in etherial solution with NH_3 gas, evaporating and extracting the residue at 0° with alcoholic NH_3, when only the salts of the liquid acid go into solution. (The reporter [Fahrion] does not regard this method as exact, for he himself has shown that ammon. stearate and palmitate are not insoluble in cold alcohol.) E. Erdmann (*Chem. Zentralbl.*, 1911, II, 1677) separates oleic, linolic and linolenic acids by fractional crystallization of their zinc salts from alcohol; the oleate is difficultly soluble, the linolate easier, the linolenate easiest. P. Werner (*Dissertation*, Berlin, 1911) made a series of laborious experiments in the endeavor to utilize the new reactions of cholesterin and phytosterin for the detection of small amounts of animal fats in vegetable oils, but with negative results. *Soaps.*—The use of soap powder and liquid soaps is increasing. Petroleum hydrocarbons are merely mechanical constituents in soaps and cannot exceed 10 per cent. Shukoff and Schestakoff (*Chem. Ztg.*, 35, 1027) found the efficient cleans-

Digitized by Google

ing power of soaps in the following order: tallow soap (maximum), liquid vegetable oil and olein soaps, cocoanut and palmnut oil soaps, resin soap. The most favorable concentration is 0.2 to 0.4 per cent. Wittels and Welwart (*Seifensieder Ztg.*, 38, 395) have investigated dressing oils. Those which are not sensitive to hard water such as monopol soap, contain more organic combined H_2SO_4 and more alkali. They are less sensitive to acids and their solutions are not pptd. by mg. salts. They also have a high solvent action upon hydrocarbons. They may often contain mineral oils, nor is their solubility in water a proof to the contrary. W. J. K.

PATENTS.

Oil-testing Machine. British Patent No. 7,616. OELWERKE STERN-SONNEBORN, Hamburg, Germany.

Buffing Roll. British Patent No. 7,317. W. H. STAYNES, Leicester, England.

Leather Manufacture. British Patent No. 7,091. CHEMISCH-TECHNOLOGISCHE STUDIENGES, Hersfeld, Germany.

The water that is absorbed by skins in the usual preliminary soaking, liming, bating, etc., is removed by means of alcohol, acetone, or other water-displacing agent, and the tanning is completed with a solution of a tanning agent in a water-displacing agent. As an example, the wet skins are soaked for 24 hours in alcohol of 50-60 per cent. strength and the adhering liquid is removed as far as possible without great pressure. Successive immersions for 24 hours are then made in alcohol of 70, 80, 90, and 96 per cent., six to eight changes usually sufficing. The skins are then dried below 40° C., and are tanned in a mixture of extract in alcohol of 96 per cent. strength. The skins are subjected to pressure occasionally during the tannage, which is completed within six hours. A final treatment in an aqueous tanning solution may be employed.

Leather-Glazing Machine. British Patent No. 7,068. W. B. TURNER, Melrose, Mass.

Processes and Materials for Treating Hides and Skins. British Patents Nos. 6,795 and 6,796. J. FORSTER, Warrington, England. These patents relate to a method of leaching in which water flows on to nearly spent material, and the liquor is drawn off from the new material, but instead of employing the usual method of rotation, the flow of liquid is through a fixed circuit, and each time a leach is pitched, all the other leaches are stepped up by transferring the material from each one to that next in the series. It is proposed to do this by having the material in a cage, and lifting and dumping the cage bodily. The second patent covers the method of tanning by which successively stronger liquors are used. The liquors flow by gravity from one pit to the next, while the hides must be moved.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII OCTOBER, 1912 No. 10

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, } . . . . . Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

DIED

In New York, August 16, 1912, August M. Kilp.

ELECTIONS.

ACTIVE.

Victor H. Kadish, 658 Commerce St., Milwaukee, Wis.

Jerome S. Rogers, Leather and Paper Laboratory, Bureau of Chemistry, Washington, D. C.

Sydney A. Beggs, 620 Main Street, Woburn, Mass.

ASSOCIATE.

Herbert E. Cox, 287 Richmond Ave., Buffalo, N. Y.

Max Meltsner, 447 E. 3d. Street, Williamsport, Pa.

Carlos Lascano, Barranquila, Colombia, South America.

Digitized by Google

CHANGES OF ADDRESS.

Albert K. Comins to 6 Park Ave., Wakefield, Mass.

S. Theodore Bittenbender to care of C. F. Austin, 85 Devonshire Street, Boston, Mass.

NINTH ANNUAL MEETING.

The ninth annual convention of the American Leather Chemists Association will be held in Washington, D. C., December 5, 6 and 7, 1912.

H. C. REED,
Secretary.

THE REACTION BETWEEN SODIUM THIOSULPHATE AND A MIXTURE OF POTASSIUM BICHROMATE AND SULPHURIC ACID. A CONTRIBUTION TO THE CHEMISTRY OF CHROME TANNAGE.*

By Prof. Edmund Stiasny and B. M. Das.

Introduction.—In the so-called two-bath chrome tannage the hides or skins are first treated with a solution of potassium bichromate containing various amounts of mineral acid; the bichromate acid which is taken up by the hide is subsequently reduced in a second bath, the reducing agent being in nearly all practical cases sodium thiosulphate. The products of reduction are basic chromium sulphates, and it has been shown in a previous paper[1] that even by the use of hydrochloric acid basic chromium sulphates (and not basic chromium chlorides) are the tanning principle, the oxidized thiosulphate providing the necessary sulphate ions. Hence, in order to simplify the investigation of the second bath, sulphuric acid can be used instead of hydrochloric acid.

There are three different ways of making the reaction mixture.

(1) The bichromate solution is mixed with a sufficient quantity of sulphuric acid, and thiosulphate solution is added to this mixture until the reduction is complete. It is this mode of action of the three reagents which has been studied in the present paper.

(2) The bichromate solution is mixed with the thiosulphate

* *Journal of the Society of Chemical Industry*, Aug. 31, 1912, Vol. 31, pp. 753-9.

[1] *Der Gerber*, 1902, No. 664.

Digitized by Google

solution and sulphuric acid is added to this mixture. The processes going on in this case are quite different from those in case 1, brown chrome-dioxide (*i.e.*, insoluble basic chromic chromate) being first formed, and then gradually converted into chromic sulphate by means of the mineral acid. These processes deserve more elucidation[2], as they play an important part whenever insufficient acid is present in the second bath.

(3) The thiosulphate solution is mixed with sulphuric acid, and the bichromate solution is added to this mixture. Even this mode of procedure is of practical interest, because a number of chrome tanners put the hides or skins, when they come from the first bath, into such a freshly made mixture of thiosulphate and mineral acid.

There are obviously two processes to distinguish in this case, viz., the action of acid on thiosulphate, and the subsequent reducing action of the products of this action on bichromate.

As regards the first part of the process, one usually finds the following equation given to illustrate the action of sulphuric acid on thiosulphate:—

$$Na_2S_2O_3+H_2SO_4=Na_2SO_4+SO_2+S+H_2O.$$

This reaction, though it explains the main part of the process does not cover the whole problem, as other reactions are going on simultaneously, and—under certain conditions—can play a very considerable part in the whole process. These side reactions are characterized by the formation of sulphuretted hydrogen[3] (which can be observed by its smell) and of sodium tetrathionate[4] and sodium pentathionate.[5]

G. Vortmann (*loc. cit.*) tries to explain this complicated reaction by assuming that thiosulphuric acid is formed as a primary product of the action of mineral acid on sodium thiosulphate. This thiosulphuric acid then decomposes into sulphur dioxide, sul-

[2] See also Kopp, *Chemical News*, 1864, **2**, p. 16.

[3] See G. Vortmann, *Ber.*, 1888, **22**, 2307; also Antonio Longi, *Gazz. chim.*, 1896, 119, and Seyewetz and Chicaudard, *Bull. Soc. Chim.*, 1895, **13**, (3), 11, who explain the process by dividing it into two parts, *viz.*, $2Na_2S_2O_3 + H_2SO_4 = Na_2SO_4 + 2NaHS_2O_3$, and $2NaHSO_3 = Na_2SO_4 + SO_2 + H_2S + S$.

[4] G. Vortmann, *loc. cit.*

[5] G. Chancel and E. Diacon, *Comptes rend.*, 1863, **56**, 710.

Digitized by Google

phuretted hydrogen and oxygen, the latter oxidizing either the before-named products or the thiosulphuric acid present in excess. The formation of sulphur, sulphuric acid[6], and tetrathionic acid is thus explained:—

$$Na_2S_2O_3+H_2SO_4=H_2S_2O_3+Na_2SO_4$$
$$H_2S_2O_3=SO_2+H_2S+O$$
$$H_2S+O=H_2O+S \text{ (main reaction)}$$
$$SO_2+O=SO_3$$
$$2H_2S_2O_3+O=H_2S_4O_6+H_2O.$$

Vortmann found up to 20 per cent. of the thiosulphate converted into tetrathionic acid. It may be mentioned that this formation of tetrathionic acid as well as of other thionic acids can be explained by the secondary action of the sulphur dioxide formed on thiosulphate. According to Villiers[7] this reaction can be expressed by the equation, $2Na_2S_2O_3+3SO_2=Na_2S_4O_6+Na_2S_3O_6$.

Anyhow, the action of mineral acids on sodium thiosulphate is by no means a simple process. Some experimental work may perhaps be mentioned here that was carried out by one of us five years ago in conjunction with Mr. M. Bachorz, when studying the influence of a small amount of arsenious acid on this reaction. The results were surprising, as tetrathionates form the principal product of the reaction if a small amount of arsenious acid is added to the hydrochloric acid, while an acid free from arsenic produces but very small amounts of tetrathionates. This explains the bad results, sometimes obtained by practical chrome tanners, who use a hydrochloric acid with considerable arsenic in it for two-bath tannage.

Working Hypothesis.—As has been mentioned above, our present paper will only deal with the reaction (or reactions) going on, when thiosulphate is allowed to act upon a mixture of bichromate and sufficient sulphuric acid. A previous paper[8] led us to expect that this process is a rather complex one, and we were prepared to find it consist of several single processes, the nature of which we wished to investigate. *A priori* there are three different

[6] Vaube, (*Ber.*, 1889, **22**) claims that sulphuric acid is one of the products, but Vortmann could not confirm this statement.

[7] *Comptes rend.*, 1889, **108**, 402; see also Berthelot, *Comptes rend.*, 1889, **108**, 971, and Hans Hertlein, *Zeit. phys. Chem.*, 1896, **19**, 287.

[8] Stiasny, *Collegium*, 1908, p. 345.

Digitized by Google

ways of oxidizing sodium thiosulphate, which have to be considered in discussing possible explanations of the process.

(a) $2Na_2S_2O_3+O=Na_2S_4O_6+Na_2O$

(b) $Na_2S_2O_3+4O=Na_2SO_4+SO_3$

(c) $Na_2S_2O_3+O=Na_2SO_4+S$.

Equation (a) illustrates the mildest form of oxidation, as we find it in the action of iodine or ferric chloride.[9] Equation (b) shows the most energetic form of oxidation, as produced by nitric acid, *aqua regia,* and also by potassium permanganate,[10] and of iodine in strongly alkaline solution.[11] Equation (c) indicates any oxidation of thiosulphate, in which the sulphur dioxide liberated by the action of a mineral acid acts as the reducing agent. There may also be processes in which thiosulphate is directly oxidized in this way.

If we assume that one or more of these three equations are needed for the explanation of the action of thiosulphate on a mixture of potassium bichromate, and sulphuric acid, and if in the above equations we substitute for oxygen such a mixture, then we arrive at the following three equations, which have to guide us in our subsequent investigation:

(a) $K_2Cr_2O_7+6H_2SO_4+6Na_2S_2O_3=$
$K_2SO_4+2CrOHSO_4+3Na_2S_4O_6+3Na_2SO_4+5H_2O$.

(b) $4K_2Cr_2O_7+9H_2SO_4+3Na_2S_2O_3=$
$4K_2SO_4+8CrOHSO_4+3Na_2SO_4+5H_2O$.

[12](c) $K_2Cr_2O_7+3H_2SO_4+3Na_2S_2O_3=$
$K_2SO_4+2CrOHSO_4+3Na_2SO_4+3S+2H_2O$.

Preliminary Qualitative Examination.—First of all some qualitative experiments were made in order to obtain information on the general course of the reactions, and to find out the relative

[9] Popp, *Zeit. Chemie*, 1870, (2), 6, p. 330.

[10] Bruegelmann, *Zeit. analyt. Chemie.*, 1884, 24.

[11] Abel, *Zeit. anorg. Chemie*, 1902, 74, 395.

[12] Equation (c) can, as has been mentioned above, be divided into two processes, *viz.*, the action of acid on thiosulphates, and the subsequent action of the sulphur dioxide thus produced on the bichromate.

$3Na_2S_2O_3 + 3H_2SO_4 = 3Na_2SO_4 + 3SO_2 + 3S + 3H_2O$

$K_2Cr_2O_7 + 3SO_2 + H_2O = K_2SO_4 + 2CrOHSO_4$

$K_2Cr_2O_7 + 3Na_2S_2O_3 + 3H_2SO_4 =$
$3Na_2SO_4 + K_2SO_4 + 2CrOHSO_4 + 3S + 2H_2O$.

Digitized by Google

amounts of reagents necessary to produce complete reduction, without excess of any of them, but with sufficient acid to avoid the separation of insoluble basic chromic sulphate. Supsequently the time was observed, necessary for complete reduction, and the influence of solution, excess of acid and of thiosulphate on the speed of the process. These qualitative tests were made with normal potassium bichromate, normal sulphuric acid, and half-normal thiosulphate, the bichromate solution being first added to sulphuric acid and diluted to the desired degree with water, after which the thiosulphate solution was run in quickly and shaken up. The end of the reduction, which was carried out at ordinary room-temperature, was shown by the following reaction, which indicates unreduced bichromate even in presence of thiosulphate. Five to ten drops of the reaction mixture were placed in a test tube, and after adding ammonia until slightly alkaline, the mixture was heated to boiling, filtered, and the filtrate slightly acidified with acetic acid, using a drop of phenolphthalein, as indicator;[13] then some starch solution was added and any thiosulphate present removed by the careful addition of a few drops of $N/10$ iodine solution, the small excess of which was again eliminated by a few drops of very dilute (about $N/100$) thiosulphate solution. The decolorized solution was now acidified with hydrochloric acid, and any unreduced bichromate thus allowed to liberate iodine from the potassium iodide (previously formed by the first solution of iodine).

Only a small selection of these qualitative tests is collected in table I., but sufficient to justify the following conclusions:—

(1) Considerable time is necessary for complete reduction under the working conditions; hence a quantitative study of the process seems hopeful.

(2) Increased dilution diminishes the speed of the reaction.

(3) Excess of thiosulphate increases the speed of the reaction.

(4) Excess of sulphuric acid seems to accelerate the early stages of the reduction (change of color from red to green), but

[13] A small excess of acetic acid is harmless, and no reaction between bichromate and thiosulphate or between bichromate and potassium iodide is started in the time given.

Digitized by Google

considerably retards the complete reduction. This behavior rather favors the expectation of complexity in the reaction.

(5) In no case could separation of sulphur be observed, except where both acid and thiosulphate were used in excess.

(6) A slight though distinct smell of sulphuretted hydrogen was noticeable in all cases.[14]

To obtain a complete understanding of the process, however, it was necessary to have a quantitative analysis of the reaction mixture at various stages of the process. Such a following up of a process made it necessary to stop the reaction at any desired moment, and to discover means of determining the unreduced bichromate, reduced chrome salts, free sodium thiosulphate, and tetrathionate which may be present in the reaction mixture.

TABLE I.

Normal potassium bichromate cc.	Normal sulphuric acid cc.	Water cc.	Semi-normal thio-sulphate cc.	Time necessary for complete reduction
10	10	0	13	5 days
10	10	100	13	14 "
10	10	0	11	15 "
10	10	0	12	15 "
10	10	0	13	5 "
10	12	0	12	13 "
10	12	0	13	12 "
10	12	0	14	20 hrs.
10	10	100	13	14 days
10	15	100	13	24 "
10	20	100	13	28 "
10	12	0	14	20 hrs.
10	13	0	14	3 days
10	14	0	14	5 "

For stopping the reduction process, the following three methods were found available:—

1. Addition of alkali.
2. Precipitation of the chromates by barium salts.
3. Rapid reduction of the chromates by ferrous salts.

The effect of strong dilution can also be utilized. This does not stop the process, but makes it so slow that aliquot parts of the mixture can be taken for single determinations, without allowing the time of manipulation to influence the composition of the mixture to any perceptible extent.

[14] See also Longi, *loc. cit.*

Digitized by Google

Quantitative Methods of Analysis of the Reacting Mixture.—It must be remembered that the following substances may be present in the same mixture: Potassium bichromate, bichromic acid, sulphuric acid, basic chromic sulphates, thiosulphate, tetrathionates, sulphates of sodium and potassium, finally sulphur (in colloidal solution) and pentathionate.

Determination of the Reduced and Unreduced Chromium Compounds.—An aliquot part of the reacting mixture (after diluting to 500 cc.) was pipetted into a beaker containing dilute ammonia, which stops the reduction and precipitates the reduced chromium as chromium hydroxide. The gravimetric estimation of the latter is then carried out in the ordinary way. The amount of unreduced chromium can be calculated by difference, knowing the amount of bichromate originally taken for the experiment. It can also be determined directly by the method described in the qualitative examination, using the filtrate of the ammonia precipitation to which after slight acidification with acetic acid a little iodine is added to remove thiosulphate, and (after eliminating any excess of iodine) acidifying with hydrochloric acid and finally titrating the iodine which is thus liberated.

Determination of Unconsumed Thiosulphate.—An aliquot part of the reacting mixture (made up to 500 cc.) was pipetted into a beaker containing a mixture of about equivalent parts of ammonia and ammonium chloride. The mixture will stop the reaction and precipitate the chromium, but its alkalinity is too slight to act on the tetrathionate which with distinctly alkaline reagents is converted into thiosulphate. By slightly acidifying with acetic acid a clear solution is obtained, from which we hoped to precipitate the chromates (and sulphates) by means of barium chloride and to determine the thiosulphate in the filtrate of the above precipitation by titrating with $N/10$ iodine. The results, however, were always too low, and it was found that the barium sulphate *in statu nascendi* caused this loss by absorbing considerable amounts of thiosulphate. Similar observations of adsorption occlusion of different substances by barium sulphate are well known.[15]

[15] Richards, *Zeit. phys. Chem.*, 1904, 29. Kund Estrup and E. B. Anderson, *Kolloid-Zeitschr.*, 1912, **10**, 161.

Digitized by Google

Table II proves that only when barium sulphate is formed in the liquid are such losses observed.

TABLE II.

To 5 cc. N/10 thiosulphate solution were added	cc. N/10 iodine Used	Expected
Chrome alum solution	5	5
Barium chloride solution	5	5
Freshly precipitated chromium hydroxide	5	5
A mixture of ammonia and ammonium chloride	5	5
A mixture of ammonia, ammonium chloride, and chrome alum	5	5
Chrome alum and barium chloride	4.5	5
Sodium sulphate and barium chloride	2	5
Freshly precipitated barium sulphate	5	5

The difficulty which arose by this adsorption of thiosulphate could be avoided by adding a known amount of $N/10$ iodine to the solution before precipitating with barium chloride. The excess of iodine could thus be titrated back with $N/10$ thiosulphate, without filtering off the insoluble barium salts. Table III shows the correctness of this method by some figures, chosen from a much larger number of experiments that were carried out with equally good results.

TABLE III.

	The analyzed mixture was made up of	cc. N/10 thiosulphate Used	Expected
1.	5 cc. N/10 thiosulphate 2 cc. chrome alum solution (10 per cent.)	5.0	5.0
2.	1 cc. N-potassium bichromate 2 cc. chrome alum solution 5 cc. sodium tetrathionate solution 5 cc. N/10 thiosulphate, added after neutralizing the above mixture with ammonia and ammonium chloride	5.0	5.0
3.	20 cc. N-potassium bichromate 24 cc. N-sulphuric acid 16 cc. water 24 cc. N/2 thiosulphate After standing one hour	1.5	Duplicate: 1.5

Example 3 illustrates the close agreement of duplicates, made on actual reaction mixtures.

The unconsumed portion of thiosulphate, which can be thus determined, deducted from the amount of thiosulphate originally

Digitized by Google

taken for the experiment, gives the figures for the consumed (oxidized) thiosulphate.

Determination of the Sodium Tetrathionate Formed During the Process.—Our method was based on the action of a strong potassium carbonate solution on sodium tetrathionate. Gutmann,[16] who studied the action of different alkalis on tetrathionate, expresses the action of potassium carbonate by the following equation:—

$$4Na_2S_4O_6+5Na_2CO_3=7Na_2S_2O_3+2Na_2SO_4+5CO_2.$$

Our experiments, which were carried out by heating 100 cc. of the solution containing tetrathionate with 30 cc. of a 40 per cent. solution of potassium carbonate for one hour on the steam bath, allowing to cool, acidifying with a 25 per cent. acetic acid, and titrating with iodine, lead us to a different result. In all cases we found that the iodine value of the solution after such treatment agreed with the amount of iodine necessary to produce the tetrathionate originally present. Table IV gives a few of the many similar results which we obtained.

It would not be correct to explain the agreement between the first and second columns in Table IV by assuming that each mole-

TABLE IV.

cc. N/10 iodine for obtaining the tetrathionate starting from thiosulphate	cc. N/10 iodine* used according to the method given above	cc. N/10 iodine calculated according to Gutmann's equations
9.9	10.0	8.65
10.0	10.15	8.75
10.0	10.15	8.75

cule of tetrathionate is converted into two molecules of thiosulphate. This becomes clear if the treatment with potassium carbonate is repeated several times, the iodine value showing a gradual diminution, which surely cannot be explained on the above hypothesis. We have, however, not investigated the chemical

[16] *Ber.*, 1908, **41**, 300.

* The values of this column are slightly higher than those of the first column; this can be explained by the fact that the thiosulphate from which we started contained traces of tetrathionate. When 10 cc. of this thiosulphate solution was treated with potassium carbonate in the above way, the number of cc. N/10 iodine finally used was also 10.15.

Digitized by Google

nature of these reactions,[17] nor have we gone into the question of the discrepancies between Gutmann's results and our own.

For the purpose of this paper, we were satisfied with the behavior of tetrathionate when first treated with potassium carbonate under the above conditions. As a supplementary proof of the correctness of the results in Table IV we made a similar experiment starting from pure sodium tetrathionate[18] twenty-five cc. of our tetrathionate solution gave on oxidizing with bromine (in alkaline solution) and precipitating with barium chloride, 0.3862 and 0.3866 gram of barium sulphate corresponding to 0.11205 gram of sodium tetrathionate. 25 cc. of the tetrathionate solution, after the treatment with potassium carbonate required 8.3, 8.3, 8.35, 8.35 cc. $N/10$ iodine; and calculating from that on tetrathionate, assuming that $1Na_2S_4O_6$ corresponds to 2 I, the figure 0.112 gram is found, which is in very good concordance with the figure found gravimetrically.

Having thus convinced ourselves of the reliability of the method, we had to apply it to our reaction mixtures. The reduction was in this case stopped by quickly reducing the chromates by means of ferrous sulphate and a little sulphuric acid. It remains now to remove the reduced chromium together with the iron salts and to determine the tetrathionate by the potassium corbonate method. Several attempts to do both simultaneously did not give satisfactory results, and we finally adopted the following mode of procedure, which proved quite reliable. The solution to be analyzed was pipetted into a 200 cc. flask and reduced with ferrous sulphate and sulphuric acid; after a few minutes standing, a 10 per cent. sodium hydroxide solution was care-

[17] The action of potassium carbonate on tetrathionate possibly leads to a mixture of thiosulphate and other products, reacting with iodine so that the total iodine consumed agrees with the iodine value of the tetrathionate from which we started. But while the thiosulphate is reconverted into tetrathionate, the other products react in different ways (being perhaps oxidized to sulphates), so that on repeating the process a lower iodine value will be found.

[18] This salt was prepared according to "Laboratory Methods of Inorganic Chemistry," by Biltz, Hall, and Blanchard, p. 132. It is stated there that the amount of water of crystallization varies, but is approximately $2H_2O$ for $Na_2S_4O_6$. We found 10.4 per cent. water in our salt, while $Na_2S_4O_6 + 2H_2O$ requires 11.6 per cent.

Digitized by Google

fully added from a burette until a few drops phenolphthalein (previously added) showed a slight alkaline reaction. Then the slight soda excess was removed by a drop or two of hydrochloric acid and subsequently the solution made faintly alkaline with ammonia.[19] After making up to the mark with water, thoroughly mixing, and filtering, 100 cc. of the filtrate were heated for one hour on the steam bath together with 30 cc. of a 40 per cent. potassium carbonate solution. The liquid after cooling and slightly acidifying with acetic acid was titrated with $N/10$ iodine. Table V. gives some results obtained by reducing various amounts of bichromates by means of ferrous sulphate and sulphuric acid, adding tetrathionate and applying the above method of analysis.

TABLE V.

cc. normal bichromate	cc. tetrathionate solution	cc. N/10 iodine	
		Used	Calculated
5	25	8.3	8.3
10	25	8.3	8.3
15	25	8.3	8.3
15	25	8.3	8.3

Mixtures used for analysis.

cc. N-bichromate	cc. N-sulphuric acid	cc. water	cc. N/2 thiosulphate
20	24	16	24 (see Table VI.)
20	24	100	24 (see Table VII.)
20	24	300	24 (see Table VIII.)
20	48	100	24 (see Table IX.)
20	24	100	48 (see Table X.)

In addition to the above tests the following experimental proof was obtained of the correctness of the method:— 20 cc. N-bichromate were mixed with 24 cc. N-sulphuric acid and 24 cc. $N/2$ thiosulphate added, and the mixture after the addition of 50 cc. tetrathionate solution allowed to stand for 3 hours. Another mixture was made in analogous way with 50 cc. of water instead of the tetrathionate solution. Both liquids were analyzed and the difference of the tetrathionate figures found by the above method was in very good concordance with the figure corresponding to 50 cc. of the tetrathionate solution.[20]

[19] By this mode of procedure a complete precipitation of chromium and iron salts is obtained, in such form that filtration is easy.

[20] This result also shows that the tetrathionate formed during the process is an end product and is not attacked by the chromate-sulphuric acid mixture. This is also confirmed by J. Myers (*J. prakt. Chem.*, 1870, **108**, 123); a different view is held by A. Longi, *loc. cit.*

Digitized by Google

Moreover, it was found that in all cases where duplicates have been made, these duplicates were in good concordance.

Application of the Above Methods to the Quantitative Analysis of the Reacting Mixture.—The following mixtures were prepared by running the solutions in the order given below from burettes into a 500 cc. flask, which after well mixing is kept at a low temperature (surrounded by a running stream of cold water) for different intervals, viz., 5 mins., 20 mins., 60 mins., 4 hours, 24 hrs. After these times the flasks were filled up to the mark with water, well shaken and aliquot parts taken for the quantitative determinations as described above. One mixture was diluted and analyzed immediately after its preparation.

The analytical figures obtained are collected in the Tables VI—X and need no further explanation. It may however, be mentioned that nearly every figure of Table VII have been verified by duplicate analysis while in the other tables such duplicates have only been made occasionally. The last column of these tables shows what portion of the bichromate (in percentage of the original amount) was reduced. From this column it can be seen that the greater part of the process goes on very rapidly, so that 70—80 per cent. of the bichromate is reduced immediately after mixing the components. It is the remaining 20—30 per cent. of the process which goes on with a measurable and gradually diminishing speed. It can further be seen from this column, that dilution lowers the speed of both the initial portion and of the later phases of the reaction. Excess of thiosulphate, on the contrary, increases the speed of both parts of the reaction, while excess of sulphuric acid distinctly accelerates the initial portion of the reaction and considerably retards the completion of the process. (The qualitative observations had already shown this; see p. 754.)

In Table XIb the figures which show these regularities are put together.

As to the analytical figures of Tables VI—X, the first question to be answered is whether these figures agree with the assumption of one single equation, or if they make it necessary to assume that the process is a complex one, consisting of two or more single reactions. From Table XIb it can be seen that the

Digitized by Google

TABLES VI.–X.

		Potassium bichromate		Thiosulphate		Tetrathionate formed in grms. of $Na_2S_2O_6$	Chromium reduced in per cent. of total chromium
		Reduced in grms. of Cr	Unreduced in grms. of Cr.	Consumed in grms. of $Na_2S_2O_35H_2O$	Unconsumed in grms. of $Na_2S_2O_35H_2O$		
Table VI.—After	0 minutes	0.0812	0.0147	0.5168	0.0784	0.2297	80.6
"	5 "	0.0845	0.0114	0.5367	0.0585	0.2393	84.9
"	20 "	0.0657	0.0103	0.5563	0.0389	0.0457	88.5
"	60 "	0.0690	0.0069	0.5724	0.0228	0.2513	90.9
"	4 hours	0.0700	0.0060	0.5875	0.0077	0.2531	92.2
"	24 "	0.0729	0.0031	0.5927	0.0025	0.2546	96.0
Table VII.— "	0 minutes	0.0528	0.0231	0.5147	0.0806	0.2223	69.6
"	5 "	0.0571	0.0188	0.5285	0.0687	0.2267	75.2
"	20 "	0.0593	0.0166	0.5446	0.0506	0.2261	78.1
"	60 "	0.0828	0.0131	0.5670	0.0282	0.2429	82.8
"	4 hours	0.0667	0.0092	0.5826	0.0127	0.2449	87.8
"	24 "	0.0698	0.0061	0.5897	0.0055	0.2477	92.0
Table VIII.—"	0 minutes	—	—	0.5119	0.0833	—	—
"	5 "	0.0559	0.0201	0.5181	0.0771	0.2199	73.6
"	20 "	0.0575	0.0184	0.5372	0.0580	0.2287	75.8
"	60 "	0.0622	0.0138	0.5597	0.0354	0.2389	81.9
"	4 hours	0.0644	0.0095	0.5801	0.0151	0.2431	87.5
"	24 "	0.0886	0.0073	0.5875	0.0077	0.2442	91.7
Table IX.— "	0 minutes	0.0581	0.0178	0.5461	0.0491	0.2484	76.6
"	5 "	0.0598	0.0162	0.5538	0.0414	0.3540	78.8
"	20 "	0.0639	0.0121	0.5711	0.0241	0.2635	84.1
"	60 "	0.0655	0.0104	0.5850	0.0102	0.2671	86.3
"	4 hours	0.0682	0.0077	0.5875	0.0077	0.2684	89.9
"	24 "	0.0683	0.0076	0.5902	0.0050	0.2697	90.0
Table X.— "	0 minutes	0.0609	0.0151	0.6305	0.5605	0.2644	80.2
"	5 "	0.0635	0.0125	—	—	—	83.6
"	20 "	0.0681	0.0078	0.6826	0.5084	0.2849	89.7
"	60 "	0.0718	0.0041	0.6900	0.5010	0.3001	94.6
"	4 hours	—	—	0.7322	0.4588	0.3193	—
"	24 "	0.0759	0.0000	0.7595	0.4315	0.3316	100.0

Digitized by Google

latter alternative is correct; the figures in this table are gram-molecules divided by the number of gram-molecules of reduced bichromate. Hence the ratio of molecules which have reacted with one another is given in this table, and it is obvious that no simple chemical reaction can explain this kind of figures. Full figures are only given for Table VII, while average figures are given for the other tables.

TABLE XIa.

Percentage bichromate reduced	Influence of dilution			Influence of excess of acid		Influence of excess of thiosulphate	
	$+16H_2O$ See Table VI.	$+100H_2O$ See Table VII	$+300H_2O$ See Table VIII	$+24H_2SO_4$ See Table VII	$+48H_2SO_4$ See Table IX	$+24Na_2S_2O_3$ See Table VII	$+28Na_2S_2O_3$ See Table X
After 0 min.....	80.6	69.6	—	69.6	76.6	69.6	80.2
" 5 "	84.9	75.2	73.6	75.2	78.8	75.2	83.6
" 24 hours....	96.0	92.0	91.7	92.0	90.0	92.0	100.0

TABLE XIb.

The figures correspond to—	Molecules bichromate reduced	Mol. thio-sulphate consumed	Mol. tetra-thionate formed
Table VII.—After 0 mins.....	1	4.00	1.63
" 5 "	1	3.87	1.53
" 20 "	1	3.85	1.53
" 60 "	1	3.79	1.49
" 4 hours.....	1	3.66	1.42
" 24 "	1	3.54	1.37
Average values for—			
Table VI	1	3.50	1.41
" VII	1	3.78	1.49
" VIII	1	3.83	1.49
" IX	1	3.77	1.60
" X	1	4.18	1.64

From the full figures corresponding to Table VII it can be seen that the two or more processes, which go on simultaneously have no constant share of the total process as this goes on. The same deduction can be shown from the full figures of the other tables.

It remains now to split up these compound reactions into their single components.

In trying to do so we come back to the three equations given in a previous paragraph, viz.:—

Digitized by Google

(a) $K_2Cr_2O_7+6H_2SO_4+6Na_2S_2O_3=$
$K_2SO_4+2CrOHSO_4+3Na_2SO_4+3Na_2S_4O_6+5H_2O.$

(b) $4K_2Cr_2O_7+9H_2SO_4+3Na_2S_2O_3=$
$4K_2SO_4+8CrOHSO_4+3Na_2SO_4+5H_2O.$

(c) $K_2Cr_2O_7+3H_2SO_4+3Na_2S_2O_3=$
$K_2SO_4+2CrOHSO_4+3Na_2SO_4+3S+2H_2O.$

TABLE XII.

The figures correspond to—	According to equation A: Mol. bichromate reduced	Mol. thiosulphate consumed	Mol. tetrathionate formed	Share of equation A in the composite reaction Per cent.
Table VII.—After 0 mins.....	0.5433	3.26	1.63	54.3
" 5 "	0.5100	3.06	1.53	51.0
" 20 "	0.5100	3.06	1.53	51.0
" 60 "	0.4967	2.98	1.49	49.7
" 4 hours....	0.4733	2.84	1.42	47.3
" 24 "	0.4567	2.74	1.37	45.7
Average values for --				
Table VI.....	0.470	2.82	1.41	47.0
" VII	0.498	2.98	1.49	49.8
" VIII	0.498	2.98	1.49	49.8
" IX.....	0.533	3.20	1.60	53.3
" X.....	0.548	3.28	1.64	54.8

Equation A is the only one which explains the formation of tetrathionate. If therefore we start from the tetrathionate figures experimentally found and calculate the bichromate, and thiosulphate which correspond to this tetrathionate, we can split up the complete reaction into equation A and a remaining part. The calculation is very simple, as equation A shows the ratio of $K_2Cr_2O_7:Na_2S_2O_3:Na_2S_4O_6$ to be 1:6:3 or 1/3:2:1; hence we have to apply to the tetrathionate figures of Table XIb the factors 2 and 1/3 in order to get the grammolecules of bichromate and thiosulphate respectively, which have reacted according to equation A. Table XII gives the figures thus calculated and the last column shows the share of equation A in the composite reaction.

The share of equation A being thus determined and eliminated, we have now to deal with the remaining part of the reaction. It must again and by similar reasoning as before be discovered if this remaining part of the reaction can be explained by a single equation.

Digitized by Google

Table XIII gives the number of molecules of thiosulphate which have reacted with one mol. bichromate, and these figures indicate that the remaining part is still a complex one.

TABLE XIII.

	In the remaining part of the reaction after eliminating equation A	
The figures correspond to—	Mol. bichromate reduced	Mol. thiosulphate consumed
Table VII.—After 0 mins.....	1	1.62
" 5 "	1	1.65
" 20 "	1	1.61
" 60 "	1	1.61
" 4 hours.....	1	1.56
" 24 "	1	1.47
Average values of—		
Table VI	1	1.28
" VII	1	1.59
" VIII	1	1.71
" IX	1	1.22
" X.....	1	1.99

Table XIII shows that there is no single molecular ratio between bichromate and thiosulphate in this remaining part of the reaction, and that the ratio is influenced by dilution, excess of acid, and excess of thiosulphate. We have now again to split up this remaining composite reaction into its components, but we have no such starting point as before, when we were able to calculate the share of the equation A from the tetrathionate figures.

Equation C would seem to present such a clue by the amount of sulphur which it contains. But no sulphur could be determined or even observed in our experiments[21] and another mode of procedure must therefore be chosen.

The two equations, B and C, to which we must return are distinguished by the different molecular ratio between bichromate and thiosulphate.

In equation B this ratio is 4:3 or 1:0.75

In equation C this ratio is 1:3.

The ratio expressed in Table XIII is in all cases between these two limits, and therefore allows us to calculate the share of B and C in the composite reaction by the following simple calcula-

[21] It will be shown later that equation C is really represented in the composite reaction, and why the sulphur escapes observation.

Digitized by Google

tion (where M is the share of B, and N the share of C in per cent.).

Example: $M+N=100$

and $0.75M+3N=1.59\times100$ (1.59 is taken from Table XIII as average value for Table VII).

Hence $M=62.7$ and $N=37.3$.

After elimination of equation A, the remaining part of the reaction is distributed between 62.7 per cent. of equation B and 37.3 per cent. of equation C.

If similar calculations are made with the other figures of Table XIII and if the share of equation A is also taken into consideration, the figures of Table XIV are obtained which show the share of the three equations A, B and C in the composite reaction.

TABLE XIV.

The figures correspond to	In the composite reaction: Share of equation A Per cent.	Share of equation B Per cent.	Share of equation C Per cent.
Table VII.—After 0 mins.....	54.3	28.0	17.7
" 5 "	51.0	29.4	19.6
" 20 "	51.0	30.3	18.7
" 60 "	49.7	31.1	19.2
" 4 hours	47.3	33.7	19.0
" 24 "	45.7	35.5	18.8
Average values of—			
Table VI.....	47.0	40.3	12.7
" VII.....	49.8	31.5	18.7
" VIII	49.8	28.7	21.5
" IX	53.3	37.3	9.4
" X.....	54.7	20.4	29.9

Before discussing the figures of Table XIV more evidence must be given for the equations B and C playing a part in the complex process. First we have to show that sulphur is formed as indicated by equation C, though this sulphur does not produce any precipitation, or even any opalescence. It can nevertheless be easily proved that sulphur has been formed. A portion of this sulphur is present in form of a colloidal solution, and the remaining and greater portion of this sulphur has reacted *in Statu nascendi* with the tetrathionate forming pentathionate.[22]

[22] This secondary reaction does not interfere with the method used for the determination of sodium tetrathionate, because the latter is reformed, when the pentathionate is treated with potassium carbonate; it then reacts further in the way described above.

Digitized by Google

To prove the presence of sulphur in colloidal solution, a mixture of 20 cc. *N*-bichromate, 24 cc. *N*-sulphuric acid, 100 cc. water and 24 cc. *N/2* thiosulphate was allowed to stand for 24 hours and then shaken out six times with carbon bisulphide. The carbon bisulphide layers were collected in a weighed flask, the solvent distilled off, and the last traces removed by a current of air; the flask was then dried in the steam oven allowed to cool in the desiccator and weighed. The residue (7.6 mg.) was proved to be sulphur not only by its appearance but also by forming sulphuric acid when oxidized with *aqua regia*.

The presence of such colloidal sulphur was to be expected from the experience of previous workers. Debus[23] found such colloidal sulphur (which he called δ-sulphur) in Wackenroder's liquid; Engel[24] stated that solutions of colloidal sulphur of considerable strength can be obtained by the action of hydrochloric acid on thiosulphate, and Raff 25 and others have recorded similar observations. Besides, it is quite possible that the presence of colloidal basic chromium sulphates increases the stability of such colloidal sulphur solutions.

The formation of pentathionate, which accounts for the greater part of sulphur formed according to equation A, could be shown by two tests. The first, given by Debus in his classical paper on Wackenroder's solution (*loc. cit.*), consists in the separation of sulphur by addition of sodium hydroxide and distinguishes pentathionate from tetrathionate and tri-thionate and from thiosulphate.

In our case we had to add an excess of sodium hydroxide in order to redissolve the chromium hydroxide primarily formed; a distinct separation of sulphur could be immediately observed and the residue after extracting with carbon bisulphide and evaporating the solvent, was easily identified as sulphur by its appearance and by burning with the well-known blue flame and the strong smell of sulphur dioxide.

Another test, used by Colefax,[26] is carried out by the addition of ammoniacal silver nitrate solution, which produces a white

[23] *Loc. cit.*

[24] *Comptes rend.*, 1891, 112, 866.

[25] *Kolloid-Zeitschrift*, 1908, 2, 318.

[26] *J. Chem. Soc.*, 1892, *Trans.*, p. 196; see also Debus, *loc. cit.*, p. 297-8.

Digitized by Google

precipitate, gradually turning black. To apply this reaction we had first to remove the reduced chromium; this was done by the mixture of ammonia and ammonium chloride which is so slightly alkaline that it does not react with the pentathionate (in the time taken by the test) but completely precipitates the chromium sulphates. The filtrate (which is obtained clear, when a little barium sulphate is added to the liquid) gives them very distinctly the above reaction with ammoniacal silver nitrate.

The pentathionate, it may be mentioned, is quite stable in acid solutions, while it is unstable in neutral ones (see also Debus), and we could get positive results with both tests applied to our reaction mixtures, even after standing for two months.

The assumption of equation C taking part in the complex reaction being proved, we thought it desirable to obtain additional evidence of the correctness of the figures in Table XIV and of the whole general explanation of the process. This independent verification is based on the fact, that the amount of sulphate produced according to the equations A, B, and C, can be calculated and this figure compared with the figure obtained by actual experiment. We see that no sulphates are fomed in equation A, further that two sulphate-ions are produced from one thiosulphate molecule in equation B and that one sulphate-ion is formed from one thiosulphate molecule in equation C. Taking now the share of A, B, and C, in any one special case it is easy to calculate the amount of sulphate formed in the mixture. The concordance of such a figure with the figure experimentally found was indeed satisfactory, considering the number of analytical examinations on which the respective figures are based. The calculated figure was 69.2 mg. SO_4, the figure actually found 64.7 mg. SO_4.

Returning now to the figures of Table XIV, the foundation of which we hope to have proved, we can state the following conclusions which may be regarded as a short summary of the results of our investigation:—

1. The reduction of a bichromate sulphuric acid mixture by means of thiosulphate can be explained as a complex process, consisting of three single reactions (see equations A, B, and C).

2. The proportional influence of these single reactions depends

Digitized by Google

on the conditions of the process, viz., dilution, amount of acid and of thiosulphate. Dilution increases slightly the share of equation A, diminishes considerably the share of B, and increases considerably the share of C (see Table XIV; average figures of VI, VII, VIII).

Excess of acid increases the share of the equations A and B and greatly diminishes the share of C (see Table XIV; average figures of VII and IX).

Excess of thiosulphate increases the share of A and especially that of C while it diminishes the share of B (see Table XIV; average figures VII and IX).

3. Seventy to eighty per cent. of the process takes place too quickly for the speed to be measured, and it is the last stages which have furnished the time measurements described in the present paper.

4. Very little sulphur is present in the reduced liquor; the sulphur formed according to equation C has to a great extent reacted upon the tetrathionate (the pentathionate thus formed being now identified) and is partially present in a colloidal form. It is very probable that most of the sulphur produced in two-bath tannage is not a product of the reduction process but of the direct action of mineral acid on thiosulphate; and it is not only the excess of acid which reacts with an excess of thiosulphate, but also the reduced chromium salts which by the neutralizing action of an excess of thiosulphate are rendered more basic.

In conclusion, we leave to others the drawing of directly practical conclusions, but express the hope that the chemical changes of the two-bath chrome tannage have been made somewhat clearer by the above investigations, and that useful methods have been elaborated for the detection and estimation of the various possible constituents of second-bath liquors.

Discussion.

Mr. G. Ward said he had noticed that potassium bichromate was sometimes mixed with ordinary alum. Was this done to moderate the intensity of the reaction, and what difference was there in the results obtained in the process with potassium bichromate and those obtained with chrome alum?

Digitized by Google

DR. H. INGLE in studying the action of water on sulphur compounds, notably on sulphur chloride, was surprised to find a colloidal form of sulphur produced together with considerable quantities of tetra- and di-thionates. He thought this sulphur might be related to that produced in Dr. Stiasny's experiments. In the standardization of sodium thiosulphate against a mixture of potassium bichromate, potassium iodide, and acid, could any error get into the results by direct action between the bichromate and thiosulphate?

MR. T. FAIRLEY asked if the differences in Dr. Stiasny's results and those of other investigators obtained when mixtures of tetrathionates and potassium carbonate were boiled, could be accounted for by differences in the degree of dilution?

Mr. J. W. COBB was surprised at the low reaction velocities in the work and asked if any general explanation of this could be given.

DR. STIASNY, in reply, said that mixtures of bichromate and alum were used when it was desired to have combination tannages. These had a great role to play in the future. The alum combined with the bichromate, forming basic aluminum sulphate and bichromic acid, both of which were taken up by the hide. The addition of chrome alum to the bichromate bath had a similar effect and produced a combined one and two-bath chrome tannage. The reaction between thiosulphate and a mixture of bichromate, acid, and potassium iodide was quite different from the reaction dealt with in the paper, as in the former case the thiosulphate reacted with the iodine previously liberated and not with the bichromate directly. There was no doubt that the basis of their iodometric analysis was correct and simple.

With regard to the action of potassium carbonate on tetrathionate, he had not gone into the question of explaining the differences in the results obtained by him and Gutmann, but intended to do so and to clear up the reactions, which took place under different conditions.

As to the slowness of the reaction, only the last 20-30 per cent. of the bichromate was reduced at a measurable rate; and months had often to elapse before completion of the reaction.

Digitized by Google

The amounts of acid or of thiosulphate (or of both) were chosen so that no excess was present, so that the final stages of the reaction, which was not an ionic reaction, were going on with minute quantities and at great dilutions.

COMPARATIVE ANALYSIS.[1]

By W. K. Alsop.

I was requested by the Council to have this committee test the "Proposed Official Method for the Analysis of Vegetable Materials Containing Tannin" embodied in the report of the committee appointed to revise the Official Method (Journal, Vol. VII, No. 6, pages 287-300).

The following samples were sent to such members of the Association as expressed a willingness to make the tests:

No. 1 Solid unclarified quebracho extract.
No. 2 Liquid chestnut extract.
No. 3 Liquid oak bark extract.
No. 4 Liquid hemlock extract.
No. 5 Liquid sulphite—cellulose extract.
No. 6 Hemlock bark.

Partial or complete reports have been received from the following collaborators:

F. Ames, Graton & Knight Mfg. Co., Worcester, Mass.
L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.
C. R. Delaney, Hanover, Pa.
R. E. Drake, Boston, Mass.
Chas. Eachus, Boston, Mass.
J. V. R. Evans, Sheboygan, Wis. W. A. Fox, Kenosha, Wis.
T. A. Faust, Newark, N. J.
Paul Hayes, Graton & Knight Mfg. Co., Worcester, Mass.
A. W. Hoppenstedt, Buffalo, N. Y.
F. M. Loveland, Dubois, Pa.
J. E. McNutt, Elk Tanning Co., Ridgway, Pa.
T. J. Mosser, Newberry, Pa.
M. F. Nichols, Knoxville, Tenn.
C. W. Norris, New York, N. Y.

[1] Report of 1912 committee.

Digitized by Google

L. M. Richeson, England Walton Lab., Harrisonburg, Va.

J. M. Seltzer, Kistler, Lesh & Co., Lock Haven, Pa.

C. C. Smoot III, North Wilkesboro, N. C. W. G. Sprinkel, North Wilkesboro, N. C.

W. R. Snell, Richwood, W. Va.

F. O. Sprague, Olean, N. Y.

G. W. Toms, Jr., Tanning Research Lab., New York, N. Y.

H. M. Johnquest, Tanning Research Lab., New York, N. Y.

Adolf Schubert, Tanning Research Lab., New York, N. Y.

W. F. Wilson, Lynchburg, Va.

R. H. Wisdom, Stamford, Conn.

The results will be found in tables 1 to 6. In making the general averages and summary, showing highest and lowest results and the maximum differences, I have omitted such figures as it seemed to me should be left out, generally because of marked variations from the balance of the tests. In the analyses represented by the general averages, the percentage of tannin is not always exactly the difference between the soluble solids and non-tannins, owing to incomplete sets of results or to ommissions.

A majority of the analysts collaborating in these tests made no comments whatever upon the proposed method and the others were generally very brief. The analysis of extracts will be discussed by paragraphs of the proposed method.

Amount and Dilution for Analysis.

Precautions taken while weighing extract for analysis are given as follows:

Liquid extracts	none, except rapidity, 6
Liquid extracts	stoppered weighing bottle, 13
Solid extracts	none, except rapidity, 10
Solid extracts	stoppered weighing bottle 10

In this connection, the following averages are given for what they are worth:

	Quebracho	Oak bark
Total solids, stoppered bottle	87.63	45.66
Total solids, no precaution	88.30	46.11

The other liquid extracts give much the same comparison. Among the results where no precaution was used is one set that is consistently much higher than the average. The figures seem

Digitized by Google

to indicate that the use of stoppered weighing bottles is the more accurate in most cases.

One analyst, Mr. Hoppenstedt, makes comments upon the proposition to allow "not less than 0.375 nor more than 0.425 gr. tannin" per 100 cc. of solution.

He says: "In my opinion, the narrowing of the limits of tannin per 100 cc. is raising greater and unnecessary obstacles to preparing an analysis according to the official method. As it is, the limitations in the present method often leave much to be desired, and comparative analyses made in various laboratories have repeatedly shown that there are greater differences in total solids than in the non-tannins."

This change is proposed as likely to bring about more uniformity in the strength of solutions and therefore more concordance in the determination of non-tannins and insolubles. I agree with the Committee as to the advisability of the change as to extracts. The more exact directions for dissolving extracts are certainly an improvement. Mr. Hoppenstedt objects to washing the strong extract solutions into cold flasks, and Mr. Smoot suggests that the method should specify that water at 85 degrees should be first poured into the flask. Probably some amount, say about 400 cc. should be specified.

Cooling.

Mr. Faust is in favor of rapid cooling but thinks the solutions should stand one hour before cooling with water at 19 degrees. He is of the opinion that "insolubles can be better controlled by this rapid cooling method." Also that the slow cooling, Par. 7 (b), should be eliminated from the method. Mr. Smoot is in favor of rapid cooling.

Mr. W. F. Wilson says: "I think much more uniform results ought to be obtained by this (rapid cooling) method, especially in very cold weather when the temperature of some laboratories goes below 20 degrees."

The results in tables 1 to 5 show, in as far as can be judged from work of this character, that the rapid cooling method can be used interchangeably with the present one (cooling over night), and that it should be incorporated in the method.

Digitized by Google

TABLE NO. I.

SAMPLE NO. 1.—QUEBRACHO EXTRACT.

	Analyst	Method of cooling solutions	Temp. of solution in morning	Time to cool to 20° C.	Total solids	Soluble solids				Insolubles	Non-tan. Chroming 24 hrs.				Non-tan. Chroming 1 hr.				Tannin %		Temp. of oven during drying of residues	
						%	Highest temp. on filter	Time to collect filtrate	Appearance of filtrate		Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	%	%	Moisture in hide	Wet hide used = dry hide	Appearance of filtrates	Chroming 24 hrs.	Chroming 1 hour		
			Deg.	Min.	%		Deg.	H. M.		%	%	grms.				%	grms.				Deg.	
1	F. Ames	Rapid		60	87.43	80.24	21	1 32	Bril.	7.19	72.96	12.70	Bril.	6.10	5.90	72.79	12.79	Bril.	74.14	74.34	99.7	1
		Slow	20		87.54	80.23	20.5	2 43	Bril.	7.31	72.96	12.70	Bril.	6.04	6.30	72.79	12.79	Bril.	74.19	73.93		
2	L. A. Cuthbert	Rapid		80	88.05	82.11	23.5	1 15	Clear	5.94	72.6	12.52	Clear	6.68	6.52	72.25	12.82	Clear	75.43	75.59	98	2
		Slow	22.5		87.97	81.26	23.5	1 20	Clear	6.71	72.6	12.52	Clear	6.78	6.26	72.25	12.82	Clear	74.48	75.00		
3	C. R. Delaney	Rapid		30	91.00[1]	83.30[1]	23	2 00	Clear	7.70	—	—	—	—	7.00	76.67	11.67	Clear	—	76.30[1]	99	3
		Slow	22		91.00[1]	85.50[1]	23	2 00	Opal	5.50[1]	74.67	12.67	Clear	7.20[1]	—	—	—	—	78.30[1]	—		
4	R. E. Drake	Rapid		20	86.68	79 83	21	0 50	Bril.	6.85	—	—	—	6.32	6.18	—	—	—	73.51	73.65	99	4
		Slow	23		86.77	78.76	21	1 00	Bril.	8.01				6.09	6.25				72.67	72.51		
5	C. Eachus	Rapid		20	86.69	79.93	21	1 00	Opal	6.76	73.90	12.53	Clear	5.93	5.78	77.64	12.65	Clear	74.00	74.15	99	5
		Slow	22		86.84	78.84	21	0 50	Opal	8.00	73.90	12.53	Clear	5.65	5.78	73.64	12.65	Clear	73.19	73.06		
6	J. V. R. Evans	Rapid		80	88.46	80.64	21	1 12	Opal	7.82	73.35	12.26	Bril.	6.81	6.75	74.00	12.14	Bril.	73.83	73.89	98.5	6
	W. A. Fox	Slow	20		88 40	79.91	21	1 12	Opal	8.49	73.35	12.26	Bril.	6.81	6.66	74.00	12.14	Bril.	73 10	73.25		
7	T. A. Faust	Rapid		37	88.35	81.66	25	1 58	Clear	6.69	73.69	12.10	Bril.	6.69	6.38	73.75	12.08	Bril.	74.97	75.28	98	7
		Slow	25		88.09	80.82	24	1 47	Sl. op.	7.27	73.69	12.10	Bril.	6.97	6.76	73.75	12.08	Bril.	73.85	74.06		
8	Paul Hayes	Rapid		60	87.18	79.80	22	—	Sl. op.	7.38	73.34	12.53	Bril.	6.22	6.37	73.31	12.54	Bril.	73.58	73.43	—	8
		Slow	20		87.45	80.03	22		Sl. op.	7.42	73.34	12.53	Bril.	6.38	6.63	73.31	12.54	Bril.	73.65	73.40		
9	A. W. Hoppenstedt	Rapid		28	87.59	79.45	23	1 51	Sl. op.	8.34	74.30	12.59	Bril.	7.17	6.80	74.3	12 59	Bril.	72.28	72.65	98.5	9
		Slow	22		87.64[1]	77.66	23	2 23	Sl. op.	9.98[1]	74.30	12.59	Bril.	6.76	6.60	74.3	12.59	Bril.	70.90[1]	71.06[1]		
10	F. M. Loveland	Rapid		45	87.64	79.06	24	3 13	Sl. op.	8.58	74.49	12.75	Clear	6.74	6.29	74.60	12.70	Clear	72.32	72.77	97.5	10
		Slow	20		88.01	79.61	22.5	1 37	Opal	8.40	74.65	12.65	Clear	6.60	6.30	73.34	12.53	Clear	73.01	73.31		
11	J. E. McNutt	Rapid		34	88.98	80.91	22	1 15	Sl. op.	8.07	73.50	12.85	Clear	6.35	6.40	73.25	12.97	Clear	74.56	74.51	98	11
		Slow	21		88.98	81.04	22	1 25	Sl. op.	7.94	73.50	12.85	Clear	6.25	6.41	73.25	12.97	Clear	74.79	74.63		

Digitized by Google

12	T. J. Mosser	Rapid		20	88.30	80.76	21	0 50	Opal.	7.54	74.60	12.19	Clear	6.47[1]	6.25	73.20	12.33	Clear	74.29	74.51	97	12
		Slow	20		88.46	80.06	21	1 00	Sl. op.	8.40	74.60	12.19	Clear	7.24[1]	6.51	73.20	12.33	Clear	72.82	73.55		
13	M. F. Nichols	Rapid		35	87.67[1]	83.41	28	1 40	Clear	4.26[1]	72.00	12.32	Clear	7.60[1]	—	—	—	—	75.81[1]	—	100	13
		Slow	28		88.44[1]	81.89	28	1 50	Clear	6.55	70.50	12.39	Clear	7.67[1]					74.22	—		
14	C. W. Norris	Rapid		60	87.58	80.47	23.5	1 30	Clear	7.11	73.85	12.55	Bril.	5.96	5.73	73.90	12.53	Bril.	74.51	74.74	98.5	14
		Slow	24		87.65	80.18	23.5	1 25	Clear	7.47	73.85	12.55	Bril.	5.84	5.89	73.90	12.53	Bril.	74.34	74.29		
15	L. M. Richeson	Rapid		80	87.97	80.55	25.5	1 45	Clear	7.42	73.50	12.27	Clear	6.63	6.44	73.90	12.08	Clear	73.92	74.11	—	15
		Slow	22		88.42	81.23	25	1 11	Clear	7.19	73.50	12.27	Clear	6.67	6.55	73.90	12.08	Clear	74.56	74 68		
16	J. M. Seltzer	Rapid		40	88.12	81.27	25		Clear	6.85	72.26	12.90	Bril.	6.64	6.58	72.42	12.82	Bril.	74.63	74.69	98	16
		Slow	26		87.95	81.43	25		Clear	6.52	72.26	12.90	Bril.	6.61	6.63	72.42	12.82	Bril.	74.82	74.80		
17	C. C. Smoot [111] . . .	Rapid		30	87.72	81.76	23	1 45	Clear	5.96	73 90	12.27	Bril.	6.71	7.17	74.54	12.17	Bril.	75.05	74.59	98	17
	W. G. Sprinkel	Slow	27		87.98	81.47	24	1 25	Clear	6.51	73.90	12.27	Bril.	6.87	6.64	74.54	12.17	Bril.	74.60	74.83		
18	W. R. Snell	Rapid		40	87.55	79.67	24.8		Opal	7.88	70.00	15.00	Bril.	6.51	6.61	70.00	15.00	Bril.	73.16	73.06	95	18
		Slow	26		88.53	80.60	22.8	1 14	Opal	7.93	70.00	15.00	Bril.	6.49	6.64	70.00	15.00	Bril.	74.11	73.96		
19	F. O. Sprague	Rapid		20	88.16	80.86	23	1 10	Opal	7.30	74.47	12.76	Clear	5.99	5.89	75 60	12.20	Clear	74.87	74 97	99	19
		Slow	29		87.95	80.81	23	1 12	Opal	7.14	74.47	12.76	Clear	5.80	5.69	75.60	12.20	Clear	75.01	75.12		
	G. W. Toms, Jr. . . .																					
20	H. M. Johnquest . . .	Rapid		45	87.31	79.82	25	1 20	Sl. op.	7.49	73.30	12.55	Clear	5.99	6.01	73.30	12.55	Clear	73.83	73.81	99.5	20
	Adolf Schubert . . .	Slow	24		87.20	79.47	25	1 27	Sl. op.	7.73	73.30	12.55	Clear	6.00	5.90	73.30	12.55	Clear	73.47	73.57		
21	W. F. Wilson	Rapid		45	87.64	81.95	23	2 00	Opal	5.69	70 00	13.50	Clear	6.78	6.60	71.50	12.82	Clear	75.17	75.35	—	21
		Slow	21		87.76	81.10	23	1 50	Sl. op.	6.66	70.00	13.50	Clear	6.66	6.82	71.50	12.82	Clear	74.44	74.28		
22	R. H. Wisdom	Rapid		35	88.00	80.59	22	1 32	Sl. op.	7.41	72.70	12.56	Bril.	6.54	6.47	72.75	12.53	Bril.	74.05	74.12	98	22
		Slow	28		87.83	80.32	22	1 46	Sl. op.	7.51	72.90	12.46	Bril.	6.67	6 54	73.00	12.42	Bril.	73.65	73.78		
	General Average . . .	Rapid	—	—	87.92	80.82	—	—	—	7.10	—	—	—	6.51	6.39	—	—	—	74.19	74.31	—	—
		Slow			88.04	80.55				7.49				6 55	6.39				74.01	73.85		
Summary.	Highest	Rapid	—	—	88.98	82.11	—	—	—	8.58	—	—	—	7.17	7.17	—	—	—	75.43	75.59	—	—
		Slow			88.98	81 47				8.49				6.97	6.82				75.01	75.12		
	Lowest	Rapid	—	—	86.68	79.06	—	—	—	5.69	—	—	—	5.93	5.73	—	—	—	72.28	72.65	—	—
		Slow			86.77	78.76				6.51				5.65	5.69				72.67	72.51		
	Greatest Difference .	Rapid	—	—	2.30	3.05	—	—	—	2.89	—	—	—	1.24	1.44	—	—	—	3.15	2.94	—	—
		Slow			2.21	2.71				1.98				1.32	1.13				2.34	2.61		

[1] Not included in summary.

Digitized by Google

TABLE NO. II.

SAMPLE NO. 2.—CHESTNUT EXTRACT.

	Analyst	Method of cooling solutions	Temp. of solution in morning	Time to cool to 20° C.	Total solids	Soluble solids				Insolubles	Non-tan. Chroming 24hrs.				Non-tan. Chroming 1 hr.				Tannin %		
						%	Highest temp. on filter	Time to collect filtrate	Appearance of filtrate		Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	%	%	Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	Chroming 24 hrs.	Chroming 1 hour	
			Deg.	Min.	%		Deg.	H. M.		%	%	grms.			%	%	grms.				
1	F. Ames	Rapid		60	42.78	42.46	21	0 47	Clear	0.32	72.96	12 70	Bril.	13.95	13.66	72.79	12.79	Bril.	28.51	28.80	1
		Slow	20		42.77	42.52	20	0 52	Clear	0.25	72 96	12.70	Bril.	14.02	14.08	72.79	12.79	Bril.	28.50	28.44	
2	L. A. Cuthbert	Rapid		95	43.17	42.84	23	0 45	Clear	0.33	72.60	12.52	Clear	14.29	14 30	72.25	12.82	Clear	28.55	28.54	2
		Slow	22 5		43 22	42.87	23.5	0 41	Clear	0.35	72.60	12.52	Clear	14.23	14.17	72.25	12.82	Clear	28.64	28.70	
4	R. E. Drake	Rapid		—	43.08	42.75	21	1 00	Clear	0.33	—	—	Clear	14.40	14.15	—	—	Clear	28.35	28.60	4
		Slow	21		43.27	42.95	21	0 50	Clear	0.32			Clear	14.40	14.01			Clear	28.55	28.94	
5	C. Eachus	Rapid		20	42.58	42.42	21	0 30	Clear	0.16	73.90	12.53	Clear	13.80	13.86	73.64	12.65	Clear	28.62	28.56	5
		Slow	22		42.58	42.35	21	0 30	Clear	0.23	73.90	12.53	Clear	13 85	13.99	73.64	12.65	Clear	28.47	28.36	
6	J. V. R. Evans	Rapid		80	43.09	42.62	20	0 50	Clear	0.47	73.35	12.26	Clear	14.61	14.75	74.00	12.14	Clear	28.01	27.87	6
	W. A. Fox	Slow	20		43.15	42.90	20	0 45	Clear	0·25	73.35	12.26	Clear	14.66	14.67	74.00	12.14	Clear	28.24	28.23	
7	T. A. Faust	Rapid		37	42.88	42.59	23	0 54	Bril.	0.29	73.69	12.10	Bril.	14.41	14.28	73.75	12.08	Bril.	28.18	28.31	7
		Slow	25		43.12	42.59	23	0 34	Bril.	0.53	73.69	12.10	Bril.	14.44	14.25	73.75	12.08	Bril.	28.15	28.34	
8	Paul Hayes	Rapid		60	42.78	42 50	22	—	Bril.	0.28	73.34	12.53	Bril.	14.13	14.21	73.31	12.54	Bril.	28.37	28.29	8
		Slow	20		42.85	42.22	22		Clear	0.63	73.34	12.53	Bril.	14.12	14.32	73.31	12.54	Bril.	28.10	27.90	
10	F. M. Loveland	Rapid		45	42.90	42.51	24	1 12	Clear	0.39	74.49	12.75	Sl. op.	14.35	14.29	74.60	12.70	Opal	28.16	28.22	10
		Slow	20		42.96	42.63	21	0 47	Clear	0.33	74.65	12.65	Opal	14.42	14.38	73.34	12.53	Opal	28.21	28.25	
11	J. E. McNutt	Rapid		39	43.12	42.60	21.5	0 48	Clear	0.52	73.50	12.85	Clear	13.93	14.03	73.25	12.97	Clear	28.67	28.57	11
		Slow	21		43.48	43.03	21.5	0 49	Clear	0.45	73.50	12.85	Clear	13.90	14.07	73.25	12.97	Clear	29.13	28.96	

Digitized by Google

12	T. J. Mosser	Rapid		20	42.91	42.34	22	0 30	Clear	0.57	73.50	12.72	Clear	14.26	14.26	73.70	12.57	Clear	28.08	28.08	12
		Slow	21		42.81	42.16	22	0 30	Clear	0.65	73.50	12.72	Clear	14.26	14.09	73.70	12.57	Clear	27.90	28.07	
13	M. F. Nichols	Rapid		27	42.73	42.13	30	1 10	Bril.	0.60	72.00	12.32	Clear	14.66	—	—	—	—	27.47	—	13
		Slow	28		42.69	42.17	28	0 45	Bril.	0.52	70.50	12.39	Clear	14.39					27.78		
14	C. W. Norris	Rapid		60	42.86	42.56	22.5	0 40	Clear	0.30	73.85	12.55	Clear	13.88	13.95	73.90	12.53	Clear	28.68	28.61	14
		Slow	24		42 99	42.51	22.5	0 45	Clear	0.48	73.85	12.55	Clear	13.96	13.93	73.90	12.53	Clear	28.55	28.58	
15	L. M. Richeson	Rapid		80	43.06	42.58	23	0 18	Clear	0.48	73.50	12.27	Clear	14.30	14.30	73.00	12.08	Clear	28.28	28.28	15
		Slow	22		42.87	42.57	23.5	0 20	Clear	0.30	73.50	12.27	Clear	14.18	14.29	73.90	12.08	Clear	28.39	28.28	
16	J. M. Seltzer	Rapid		40	42.87	42.51	22	—	Bril.	0.36	72.78	12.66	Bril.	14.00	14.17	72.69	12.70	Bril.	28.51	28.34	16
		Slow	21		42.81	42.52	22		Bril.	0.29	72.78	12.66	Bril.	13.97	14.13	72.69	12.70	Bril.	28.55	28.39	
17	C. C. Smoot [1]	Rapid		30	43.00	42.89	23	0 40	Bril.	0.11	73.90	12.27	Clear	14.16	14.53	74.54	12.17	Clear	28.73	28.36	17
	W. G. Sprinkel	Slow	27		42.91	42.62	24	0 45	Clear	0.29	73.90	12.27	Bril.	14.16	14.35	74.54	12.17	Clear	28.46	28.27	
18	W. R. Snell	Rapid		25	43.20	43.00	22	0 30	Clear	0.20	70.00	15.00	Clear	13.63	13.92	70.00	15.00	Clear	29.37	29.08	18
		Slow	26		42.87	42.65	20.5	0 20	Clear	0.22	70.00	15.00	Clear	14.23	15 40[1]	70.00	15.00	Clear	28.42	27.25[1]	
19	F. O. Sprague	Rapid		30	43.08	42.59	23	0 30	Clear	0.49	74.47	12.76	Clear	14.15	13.89	75.60	12.20	Clear	28.44	28.70	19
		Slow	29		42.89	42.67	23	0 30	Clear	0.22	74.47	12.76	Clear	13.86	13.93	75.60	12.20	Clear	28.81	28.74	
20	Geo. Toms, Jr. . . .																				
	H. M. Johnquest . . .	Rapid		45	42.78	42 49	23	0 34	Clear	0.29	73.30	12.55	Clear	13.96	13.94	73.30	12.55	Clear	28.53	28.55	20
	Adolf Schubert . . .	Slow	24		42.55	42.32	23	0 39	Clear	0.23	73.30	12.55	Clear	13.90	13.91	73.30	12.55	Clear	28.42	28.41	
21	W. F. Wilson	Rapid		45	43.15	42.95	23	0 45	Clear	0.20	70.00	13.50	Clear	13.89	13.83	71.50	12.82	Clear	29.06	29.12	21
		Slow	21		42.91	42.67	23	0 45	Clear	0.24	70.00	13.50	Clear	14.41	14.29	71.50	12.82	Clear	28.26	28.38	
22	R. H. Wisdom	Rapid		35	42.87	42.61	21	0 42	Clear	0.26	72 70	12.56	Clear	14.20	14 10	72.75	12.53	Clear	28.41	28.51	22
		Slow	23.5		42.83	42.66	21	0 46	Clear	0.17	72.90	12.46	Clear	14.25	14.18	73.00	12.42	Clear	28.41	28.48	
	General Average . .	Rapid	—	—	42.95	42.60	—	—	—	0.35	—	—	—	14.15	14.13	—	—	—	28.45	28.49	
		Slow			42.93	42.58				0.35				14.18	14.17				28.40	28.43	
Summary	Highest	Rapid	—	—	43.20	43.00	—	—	—	0.60	--	—	—	14.66	14.75	—	—	—	29.37	29.12	
		Slow			43.48	43.03				0.65				14.66	14.67				29.13	28.96	
	Lowest	Rapid	—	—	42.58	42.13	-	—	—	0 11	—	—	—	13.63	13.66	—	—	—	27.47	27.87	
		Slow			42.55	42.16				0.17				13.86	13.91				27.78	27.90	
	Greatest Difference .	Rapid	—	—	0.62	0.87	—	—	—	0.49	—	—	—	1.03	1.09	—	—	—	1.90	1.25	
		Slow			0.93	0.97				0.48				0.80	0.76				1.35	1.06	

[1] Not included in general average.

Digitized by Google

TABLE NO. III.

SAMPLE NO. 3.—OAK BARK EXTRACT.

	Analyst	Method of cooling solutions	Temp. of solution in morning	Time to cool to 20°C.	Total solids	Soluble solids				Insolubles	Non-tan. Chroming 24hrs.				Non-tan. Chroming 1 hr.				Tanin %		
						%	Highest temp. on filter	Time to collect filtrate	Appearance of filtrate		Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	%	%	Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	Chroming 24 hrs.	Chroming 1 hour	
			Deg.	Min.	%		Deg.	H. M.		%	%	grms.				%	grms.				
1	F. Ames	Rapid		55	45.37	43.89	23	3 09	Bril.	1.48	72.96	12.70	Clear	18.74	18.69	72.79	12.79	Clear	25.15	25.20	1
		Slow	20		45.63	43.81	21	3 04	Bril.	1.82	72.96	12.70	Clear	18.71	18.82	72.79	12.79	Clear	25.10	24.99	
2	L. A Cuthbert	Rapid		105	46.18	44.72	24	1 55	Opal	1.46	72.60	12.52	Clear	19.14	19.15	72.25	12.82	Sl. op.	25.58	25.57	2
		Slow	22.5		46.02	44.51	24.5	1 55	Opal	1.51	72.60	12.52	Clear	19.04	19.41	72.25	12.82	Clear	25.47	25.10	
3	C. R. Delaney	Rapid		30	46.70	44.80	25	1 30	Clear	1.90	—	—	—	—	20.30	76.30	11.85	Clear	—	24.50	3
		Slow	24		46.70	45.00	25	1 30	Clear	1.70	72.10	13.95	Clear	20.10	—	—	—	—	24.90	—	
4	R. E. Drake	Rapid		—	45.90	44.43	22	1 30	Bril.	1.47	—	—	Opal	18.96	18.77	—	—	Opal	25.47	25.66	4
		Slow	23		45.75	44.25	—	2 00	Bril.	1.50			Opal	18.83	18.87			Opal	25.42	25.38	
5	C. Eachus	Rapid		20	45.26	43.80	21	1 00	Bril.	1.46	73.90	12.53	Opal	18.36	18.39	73.64	12.65	Clear	25.44	25.41	5
		Slow	22		45.22	43.79	21	1 00	Bril.	1.43	73.90	12.53	Opal	18.51	18.37	73 64	12.65	Opal	25.28	25.42	
6	J. V. R. Evans	Rapid		80	46.41	44.54	21	2 12	Clear	1.87	73.35	12.26	Opal	19.60	19.48	74.00	12.14	Opal	24.94	25.06	6
	W. A. Fox	Slow	20		46.31	44.46	21	1 42	Opal	1.85	73.35	12.26	Opal	19.57	19.58	74.00	12.14	Opal	24.89	24.88	
7	T. A. Faust	Rapid		37	45.92	42.82	25	1 58	Bril.	1.10	73.69	12.10	Bril.	19.43	19.24	73.75	12.08	Bril.	25.39	25.58	7
		Slow	25		46.03	44.77	24.5	2 28	Bril.	1.26	73.69	12.10	Clear	19.39	19.14	73.75	12.08	Clear	25.38	25.63	
8	Paul Hayes	Rapid		60	45.65	44.04	22	—	Bril.	1 61	73.34	12.53	Bril.	18.71	18.90	73.31	12.54	Bril.	25.33	25.14	8
		Slow	20		45.57	43.99	22		Clear	1.58	73.34	12.53	Bril.	18.63	18.85	73.31	12.54	Bril.	25.36	25.14	
10	F. M. Loveland	Rapid		45	45.65	44.00	24	3 00	Clear	1.65	74.49	12.75	Opal	19.15	19.16	74.60	12.70	Opal	24.85	24.84	10
		Slow	20		45.61	43.95	24	2 50	Clear	1.66	74.65	12.65	Opal	19.32	19.32	73.34	12.53	Opal	24.63	24.63	
11	J. E. McNutt	Rapid		41	45.87	44.20	22	1 50	Sl. op.	1.67	73.50	12.85	Sl. op.	18.89	18.89	73.25	12.97	Sl. op.	25.31	25.31	11
		Slow	21		46.06	44.15	22.5	2 05	Sl. op.	1.91	73.50	12.85	Sl. op.	18.71	18.86	73.25	12.97	Sl. op.	25.44	25.29	

Digitized by Google

12	T. J. Mosser	Rapid		20	45.51	44.24	23	2 00	Opal	1.27	74.00	12.48	Opal	19.26	19.15	73.30	12.82	Clear	24.98	25.09	12
		Slow	26		45.51	44.07	23	2 10	Opal	1.44	74.00	12.48	Opal	19.22	19.25	73.30	12.82	Clear	24.85	24.82	
13	M. F. Nichols	Rapid		24	45.72	43.85	30	2 30	Bril.	1.87	72.00	12.32	Clear	19.30	—	—	—		24.82	—	13
		Slow	28		45.75	44.23	28	2 30	Bril.	1.49	70.50	12.39	Clear	19.11					25.12		
14	C. W. Norris . . .	Rapid		60	45.91	44.29	24	1 50	Clear	1.62	73.85	12.55	Opal	18.59	18.71	73.90	12.53	Opal	25.70	25.58	14
		Slow	24		45.85	44.24	24	2 20	Clear	1.61	73.85	12.55	Opal	18.71	18.69	73.90	12.53	Opal	25.53	25.55	
15	L. M. Richeson . .	Rapid		80	46.09	44.8	24.5	1 03	Clear	1.21	73.50	12.27	Sl. op.	19.42	19.33	73.90	12.08	Opal	25.46	25.55	15
		Slow	22		46.03	44.34	25	1 55	Clear	1.69	73.50	12.27	Opal	19.39	19.48	73.90	12.08	Sl. op.	24.95	24.86	
16	J. M. Seltzer . . .	Rapid		40	45.75	44.13	22	—	Bril.	1.62	72.78	12.66	Opal	19.07	19.26	72.69	12.70	Opal	25.06	24.87	16
		Slow	21		45.66	44.27	22		Bril.	1.39	72.78	12.66	Opal	19.07	19.22	72.69	12.70	Opal	25.20	25.05	
17	C. C. Smoot III	Rapid		30	45 69	44.55	23	2 00	Clear	1.04	73.90	12.27	Clear	19.19	19.68	74.54	12.17	Clear	25.36	24.87	17
	W. G. Sprinkel . . .	Slow	27		45.86	45.68	24	1 00	Clear	1.18	73.90	12.27	Clear	19.29	19.42	74.54	12.17	Clear	25.39	25.26	
18	W. R. Snell	Rapid		30	45.60	44.32	24.8	2 10	Clear	1.28	70.00	15.00	Opal	18.81	19.19	70.00	15.00	Opal	25.53	25.13	18
		Slow	26		45.32	43.82	23.5	1 26	Clear	1.50	70.00	15.00	Opal	18 69	18.48	70.00	15.00	Opal	25.13	25.34	
19	F. O. Sprague	Rapid		30	45.57	44.09	23	1 30	Clear	1.48	74.47	12.76	Opal	19.07	18.83	75.60	12.20	Opal	25.02	25.26	19
		Slow	29		45.64	44.21	23	2 00	Clear	1.43	74.47	12.76	Opal	18.65	18.84	75.60	12.20	Opal	25.56	25.37	
	G. W. Toms, Jr. . . .																				
20	H. M. Johnquest . . .	Rapid		45	45.60	44.28	24.5	1 45	Clear	1.32	73.30	12.55	Clear	19.10	19.09	73.30	12.55	Clear	25.18	25.19	20
	Adolf Schubert	Slow	24		45.66	44.24	24.5	1 41	Clear	1.42	73.30	12.55	Sl. op.	19.07	19.05	73.30	12.55	Sl. op.	25.17	25.19	
21	W. F. Wilson	Rapid		45	45.57	44.30	23	1 20	Clear	1.27	70.00	13.50	Clear	18.58	18.55	71.50	12.82	Clear	25.72	25.75	21
		Slow	21		46.34	44.88	23	1 00	Clear	1.46	70.00	13.50	Clear	19.24	19.01	71.50	12.82	Clear	25.64	25.87	
22	R. H. Wisdom	Rapid		35	45.93	44.77	22	1 48	Clear	1.16	72.70	12.56	Clear	19.13	19.03	72.75	12.53	Clear	25.64	25.74	22
		Slow	23.5		45.88	44.63	22	2 11	Clear	1.25	72.90	12.46	Clear	19.27	19.17	73.00	12.42	Clear	25.36	25.46	
	General average . . .	Rapid	—	—	45.80	44.33	—	—	—	1.47	—	—	--	19.03	19.09	—	—	--	25.30	25.26	
		Slow			45.83	44.30				1.53				19.07	19.04				25.23	25.22	
Summary	Highest	Rapid	—	—	46.70	44.88	—	—	—	1.90	--	--	—	19.60	20.30	—	—	—	25.72	25.75	
		Slow			46.70	45.00				1.91				20.10	19.58				25.56	25.87	
	Lowest	Rapid	—	—	45.20	43.80	—	—	—	1.04	--	—	—	18.36	18.39	—	--	-	24.82	24.50	
		Slow			45.22	43.79				1.18				18.51	18.37				24.63	24.63	
	Greatest Difference .	Rapid	—	—	1.44	1.08	—	—	—	0.86	--	—	—	1.24	1.91	—	—	-	0.90	1.25	
		Slow			1.48	1.21				0.73				1.59	1.21				0.93	1.24	

Digitized by Google

TABLE NO. IV.

SAMPLE NO. 4.—HEMLOCK EXTRACT.

	Analyst	Method of cooling solutions	Temp. of solution in morning	Time to cool to 20° C.	Total solids	Soluble solids				Insolubles	Non-tan. chroming 24 hrs.				Non-tan. Chroming 1 hr.				Tannin %		
						%	Highest temp. on filter	Time to collect filtrate	Appearance of filtrate		Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	%	%	Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	Chroming 24 hours	Chroming 1 hour	
			Deg.	Min.	%		Deg.	H. M.		%	%	grms			%	%	grms.				
1	F. Ames	Rapid		60	49.95	46.13	23	3 40	Bril.	3.82	72.96	12.70	Bril.	20.45	20.57	72.79	12.79	Bril.	25.68	25.56	1
		Slow	20		49.87	46.32	23	2 45	Bril.	3.55	72.96	12.70	Bril.	20.45	20.59	72.79	12.79	Bril.	25.87	25.73	
2	L. A. Cuthbert	Rapid		110	50.55	47.38	24.5	2 57	Opal	3.17	72.50	12.52	Opal	20.96	20.93	72.25	12.82	Opal	26.42	26.45	2
		Slow	22.5		50.57	47.44	24.5	3 12		3.13	72.60	12.52	Opal	20.80	21.17	72.25	12.82	Opal	26.64	26.27	
3	C. R. Delaney	[1]Rapid		30	51 00	48.50	25	5 00	Clear	2.50											
		Slow	24		51 00	49.30	25	5 50	Clear	1.70	73.90	13.05	Clear	21.80	21.70	74.20	12.90	Clear		26.80	3
																			27.50		
5	C. Eachus	Rapid		20	49.55	45.66	21	2 00	Clear	3.89	73.90	12.53	Opal	20.55	20.63	73.64	12.65	Clear	25.11	25.03	5
		Slow	22		49.40	46.08	21	2 00	Clear	3.32	73.90	12.53	Opal	20.29	20.57	73.64	12.65	Opal	25.79	25.51	
6	J. V. R. Evans	Rapid		80	50.38	46.64	21	3 12	Bril.	3.74	73.35	12.26	Opal	21.67	21.77	74.00	12.14	Opal	24.97	24.87	6
	W. A. Fox	Slow	20		50.49	46.88	21	2 52	Bril.	3.61	73.35	12.26	Opal	21.20	21.57	74.00	12.14	Opal	25.68	25.31	
7	T. A. Faust	Rapid		37	50.39	46.92	25	4 02	Bril.	3.47	73.69	12.10	Clear	21.39	21.18	73.75	12.08	Clear	25.53	25.74	7
		Slow	25		50.26	47.09	25	3 43	Bril.	3.17	73 69	12.10	Opal	21.26	21.11	73.75	12.08	Opal	25.83	25.98	
8	Paul Hayes	Rapid		60	50.02	46.06	22	—	Bril.	3 96	73.34	12.53	Bril.	20.52	20.66	73.31	12.54	Bril.	25.54	25.40	8
		Slow	20		49.96	45.96	22		Clear	4.00	73.34	12.53	Bril.	20.55	20.55	73.31	12.54	Bril.	25.41	25.41	
10	F. M. Loveland	Rapid		45	49.84	46.74	24	3 45	Clear	3 10	74.49	12.75	Opal	21.39	21.52	74.60	12.70	Opal	25.35	25.22	10
		Slow	20		49.99	46.53	25	3 58	Clear	3.46	74.65	12.65	Opal	21.57	21.64	73.34	12.53	Opal	24.96	24.89	
11	J. E. McNutt	Rapid		38	50.27	46.65	23	2 58	Clear	3.62	73.50	12.85	Clear	20.38	20.69	73.25	12.97	Clear	26.27	25. 96	11
		Slow	21		50.27	46.83	23	3 15	Clear	3.44	73.50	12.85	Clear	20.46	20.82	73.25	12.97	Clear	26.37	26.01	

Digitized by Google

12	T. J. Mosser[1]	Rapid		20	51.06	46.13	22	1 30[3]	Clear	4.99	72.90	13.00	Clear	21.23	22.05	73.80	12.07	Clear	24.90	24.08	12
		Slow	25		50.96	46.07	23	1 45[3]	Clear	4.89	72.90	13.00	Opal	21.67	22.08	73.80	12.07	Opal	24.40	23.99	
13	M. F. Nichols[1]	Rapid		33	48.13	45.69	30	2 30	Clear	2.44	72.00	12.32	Clear	20.84	—	—	—	—	24.85	—	13
		Slow	28		48.13	46.84	28	3 05	Clear	1.29	70.50	12.39	Clear	19.78					27.06		
14	C. W. Norris	Rapid		60	49.94	46.57	24	3 00	Clear	3.37	73.85	12.55	Clear	20.02	20.49	73.90	12.53	Clear	26.55	26.08	14
		Slow	24		49.79	46.51	24	3 45	Clear	3.28	73.85	12.55	Clear	20.32	20.60	73.90	12.53	Clear	26.19	25.91	
15	L. M. Richeson . . .	Rapid		80	50.38	46.39	25.5	2 45	Clear	3.99	73.50	12.27	Opal	21.22	21.34	73.90	12.08	Opal	25.17	25.05	15
		Slow	22		50.03	46.51	25.5	2 45	Clear	3.52	73.50	12.27	Opal	21.44	21.42	73.90	12.08	Opal	25.07	25.09	
16	J. M. Seltzer	Rapid		40	49.96	46.70	22	—	Bril.	3.26	72.78	12.66	Opal	21.17	21.45	72.69	12.70	Opal	25.53	25.25	16
		Slow	21		49.89	46.58	22		Bril.	3.31	72.78	12.66	Opal	21.02	21.25	72.69	12.70	Opal	25.56	25.33	
17	C. C. Smoot III	Rapid		30	49.88	47.59	23	2 45	Bril.	2.29	73.90	12.27	Opal	21.53	22.03	74.54	12.17	Opal	26.06	25.56	17
	W. G. Sprinkel	Slow	27		50.05	47.66	24.8	2 15	Bril.	2.39	73.90	12.27	Opal	20.76	21.45	74.54	12.17	Opal	26.90	26.21	
18	W. R. Snell	Rapid		25	50.03	46.98	24.8	2 28	Clear	3.05	70.00	15.00	Opal	21.19	21.50	70.00	15.00	Opal	25.79	25.48	18
		Slow	26		49.79	46.10	23.8	2 36	Clear	3.69	70.00	15.00	Opal	20.85	18.32[2]	70.00	15.00	Opal	25.25	27 78[2]	
19	F. O. Sprague	Rapid		30	50.14	46.34	23	2 00	Clear	3.80	74.47	12.76	Opal	20.77	21.00	75.60	12.20	Opal	25.57	25.34	19
		Slow	29		50.23	46.58	23	3 00	Clear	3.65	74.47	12.76	Opal	20.46	20.89	75.60	12.20	Opal	26.12	25.69	
	G. W. Toms, Jr. . . .																				
20	H. M. Johnquest . . .	Rapid		45	49.69	46.73	25.5	2 10	Clear	2.96	73.30	12.55	Sl. op.	20.82	20.85	73.30	12.55	Sl. op.	25.91	25.88	20
	Adolf Schubert	Slow	24		49.68	46.68	26	2 34	Clear	3.00	73.30	12.55	Sl. op.	21.07	21.26	73.30	12.55	Sl. op.	25.61	25.42	
21	W. F. Wilson	Rapid		45	50.42	46.22	22	1 50	Bril.	4.20	70.50	13.27	Clear	20.88					25.34		21
		Slow	21		50.26	46.69	22	1 30	Clear	3.57	70.50	13.27	Clear	21.20	21.33	71.50	12.82	Clear	25.49	25.36	
22	R. H. Wisdom	Rapid		35	50.03	46.92	22	2 44	Bril.	3.11	72.70	12.26	Clear	21.24	21.18	72.75	12 53	Clear	25.68	25.74	22
		Slow	23.5		50.01	47.03	22	3 05	Bril.	2.98	72.90	12.46	Clear	21.37	21.24	73.00	12.42	Clear	25.66	25.79	
Summary	General Average . . .	Rapid	—	—	50.06	46.65	—	—	—	3.43	—	—	—	20.96	21.19	—	—	—	25.60	25.53	
		Slow			50.03	46.78				3.25				20.92	21.15				25.87	25.58	
	Highest	Rapid	—	—	50.55	47.59	—	—	—	4.20	—	—	—	21.67	22.05	—	—	—	26.55	26.45	
		Slow			50.57	47.66				4.00				21.67	21.64				26.90	26.27	
	Lowest	Rapid	—	—	49.55	45.66	—	—	—	2.29	—	—	—	20.02	20.49	—	—	—	24.97	24.87	
		Slow			49.40	45.96				2.39				20.29	20.55				24.96	24.89	
	Greatest Difference .	Rapid	—	—	1.00	1.93	—	—	—	1.91	—	—	—	1.65	1.50	—	—	—	1.58	1.58	
		Slow			1.17	1.70				1.61				1.38	1.09				1.94	1.38	

[1] Results omitted from summary. [2] Omitted from average and summary. [3] 50 cc. evaporated.

Digitized by Google

TABLE NO. V.

SAMPLE NO. 5.—SULPHITE CELLULOSE EXTRACT.

	Analyst	Method of cooling solutions	Temp. of solution in morning	Time to cool to 20° C.	Total solids	Soluble solids				Insolubles	Non-tan. chroming 24 hrs.				Non-tan. chroming 1 hr.				Tannin %		
						%	Highest temp. on filter	Time to collect filtrate	Appearance of filtrate		Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	%	%	Moisture in hide	Wet hide used = dry hide	Appearance of filtrate	Chroming 24 hours	Chroming 1 hour	
			Deg.	Min.	%		Deg.	H. M.		%	%	grms.			%	%	grms.				
1	F. Ames	Rapid		60	49.65	49.78	20.5	0 40	Bril.	0.13	72.96	12.72	Clear	22.95	23.69	72.79	12.79	Clear	26.70	25.96	1
		Slow	20		49.66	49.90	20	0 30	Bril.	0.24	72.96	12.72	Bril.	23.08	23.60	72.79	12.79	Clear	26.58	26.05	
2	L. A. Cuthbert	Rapid		115	50.67	50.67	23.5	0 32	Clear	0.00	72.60	12.52	Clear	22.06	23.08	72.25	12.82	Clear	28.61	27.59	2
		Slow	22.5		50.55	50.55	23.5	0 28	Clear	0.00	72.60	12.52	Clear	22.09	23.28	72.25	12.82	Clear	28.46	27.27	
3	C. R. Delaney[1]	Rapid		30	53.10	51.80	25	1 00	Bril.	1.30					24.60	74.20	12.90	Bril.		27.20	3
		Slow	24		53.10	52.20	25	1 00	Bril.	0.90	73.90	13.05	Bril.	24.40					27.80		
4	R. E. Drake	Rapid		20	49.75	49.72	22	1 00	Bril.	0.03	—	—	Clear	23.55	23.36	—	—	—	26.17	26.36	4
		Slow	23		49.83	49.78	22	0 40	Bril.	0.05			Clear	23.75	23.58				26.03	26.20	
5	C. Eachus	Rapid		20	49.33	49.31	21	0 30	Bril.	0.02	73.90	12.53	Clear	22.79	23.09	73.64	12.65	Clear	26.52	26.20	5
		Slow	22		48.95	48.87	21	0 30	Bril.	0.08	73.90	12.53	Clear	22.67	22.83	73.64	12.65	Clear	26.20	26.04	
6	J. V. R. Evans	Rapid		80	50.15	50.11	20	0 26	Bril.	0.04	73.25	12.26	Clear	24.10	25.04	74.00	12.14	Clear	26.01	26.14	6
	W. A. Fox	Slow	20		50.16	50.14	20	0 22	Bril.	0.02	73.25	12.26	Clear	24.00	24.74	74.00	12.14	Clear	25.07	25.40	
7	T. A. Faust	Rapid		37	49.74	49.74	22	0 33	Bril.	0.00	73.69	12.10	Clear	21.39	21.18	73.75	12.08	—	25.78	25.63	7
		Slow	25		49.80	49.80	23	0 27	Bril.	0 00	73.69	12.10	Opal	21.26	21.11	73.75	12.08		26.33	26.00	
8	Paul Hayes	Rapid		60	49.94	49.79	22	—	Bril.	0.15	73.34	12.53	Bril.	21.70	23.17	73.31	12.54	Bril.	28.09	26.62	8
		Slow	20		49.53	49.65	22		Clear	0.12	73.34	12.53	Bril.	21.57	22.68	73.31	12.54	Bril.	27.96	26.65	
10	F. M. Loveland	Rapid		45	49.91	50.04	24	0 32	Clear	0.13	74.49	12.75	Clear	24.20	23.64	74.60	12.70	Clear	25.71	26.27	10
		Slow	20		50.05	50.10	21	0 31	Clear	0.05	74.65	12.65	Clear	24.67	24.49	73.34	12.53	Clear	25.38	25.56	
11	J. E. McNu't	Rapid		36	50.35	50 22	22	0 37	Clear	0.13	73.50	12.85	Bril.	21.41	23.34	73.25	12.97	Bril.	28.81	26.88	11
		Slow	21		50.51	50.38	21.5	0 32	Clear	0.13	73.50	12.85	Bril.	21.43	23.33	73.25	12.97	Bril.	28.95	27.05	

Digitized by Google

12	T. J. Mosser	Rapid		20	50.13	50.10	22	0 20	Clear	0.03	72.90	13.00	Clear	23.98					26.12		12
		Slow	24		50.35	50.00	22	0 25	Clear	0.35	72.90	13.00	Clear	23.38	24.55	72.90	13.00	Clear	26.62	25.45	
13	M. F. Nichols	Rapid		24	49.68	49.59	30	1 10	Bril.	0.09	72.00	12.32	Clear	20.70	—	—	-	—	28.88	—	13
		Slow	28		49.82	49.58	28	0 33	Bril.	0.24	70.50	12.39	Opal	21.41					28.18		
14	C. W. Norris	Rapid		60	49.76	49.68	22.5	0 30	Clear	0.08	73.85	12.55	Clear	21.95	23.48	73.90	12.53	Clear	27.73	26.20	14
		Slow	24		49.76	49.59	22.5	0 30	Clear	0.17	73 85	12.55	Clear	21.53	23.50	73.90	12.53	Clear	28.06	26.09	
15	L. M. Richeson	Rapid		80	50.16	49.72	23.5	0 12	Clear	0.44	73.50	12.27	Clear	24.95	26.01	73.90	12.08	Clear	24.77	23.72	15
		Slow	22		50.10	49.69	22.5	0 14	Clear	0.41	73.50	12.27	Clear	24.64	25.45	73.90	12.08	Clear	25.05	24.24	
16	J. M. Seltzer	Rapid		40	50.09	49.95	25	-	Bril.	0.14	72.26	12.89	Opal	24.08	24.47	72.42	12.82	Opal	25.87	25.47	16
		Slow	26		50.13	50.12	25		Bril.	0.01	72.26	12.89	Opal	23.47	23.92	72.42	12.82	Opal	26.65	76.20	
17	C. C. Smoot [1]	Rapid		30	50.10	49.71	22	0 25	Bril.	0.39	73.90	12.27	Bril.	23.80	23.90	74.54	12.17	Bril.	25.91	25.81	17
	W. G. Sprinkel	Slow	27		50.14	49.94	23	0 30	Bril.	0.20	73.90	12.27	Bril.	23.57	23.85	74.54	12.17	Bril.	26.37	26.09	
18	W. R. Snell	Rapid		25	50.43	50.13	22.5	0 23	Clear	0.30	70.00	15.00	Clear	23.54	24.79	70.00	15.00	Clear	26.59	25.34	18
		Slow	26		49.94	49.78	24	0 36	Clear	0.16	70.00	15.00	Clear	23.38	24.52	70.00	15.00	Clear	26.40	25.24	
19	F. O. Sprague	Rapid		30	50.14	50.30	23	0 30	Clear	0.16	74.47	12.76	Opal	22.74	22.95	75.60	12.20	Opal	27.40	27.19	19
	Geo. Toms, Jr.	Slow	29		50.48	49.74	23	0 30	Clear	0.74	74.47	12.76	Opal	22.40	22.81	75.60	12.20	Opal	27.34	26.93	
20	H. M. Johnquest	Rapid		45	49.51	49.51	22	0 21	Clear	0.00	73.30	12.55	Clear	22.98	23.08	73.30	12.55	Clear	26.53	26.43	20
	Adolf Schubert	Slow	24		49.71	49.71	22	0 22	Clear	0.00	73.30	12.55	Clear	22.62	22.77	73.30	12.55	Clear	27.09	26.94	
21	W. F. Wilson	Rapid		45	50.00	49.85	23	0 35	Clear	0.15	70.50	13.27	Clear	24.33				—	25.52		21
		Slow	21		50.49	50.18	22	0 40	Clear	0.31	70.50	13.27	Clear	24.68	24.65	71.50	12.82		25.50	25.53	
22	R. H. Wisdom	Rapid		35	50.05	50.16	20.5	0 27	Clear	0.11	72.70	12.56	Clear	23.07	24.04	72.75	12.53	Clear	26.98	26.01	22
		Slow	23.5		49.98	50.10	20.5	0 28	Clear	0.12	72.90	12.46	Clear	23.00	23.73	73.00	12.42	Clear	26.98	26.25	
	General Average	Rapid			49.98	49.90				0 07				23.01	23.67				26.73	26.11	
		Slow	—	—	49.97	49.88	—	—	—	0 12	—	—	—	22.93	23.65	—		—	26.76	26.07	
Summary	Highest	Rapid			50.67	50.67								24.95	26.01				28.88	27.59	
		Slow	—	—	50.55	50.55	-	-	-	-	-	-	-	24.68	25.45	—	—	-	28.95	27.27	
	Lowest	Rapid			49.33	49.31								20.70	21.18				24.77	23.72	
		Slow	-	-	48.95	48.87	-	-	-	-	-	-	-	21.20	21 11	-		—	25.05	24.24	
	Greatest Difference	Rapid			1.34	1.36								4.25	4.83				4.11	3.87	
		Slow	—	—	1.60	1.67	-	-	-	-	-	-	-	3.42	4.34	—	-	-	3.90	3.03	

[1] Results not included in average or summary.

Digitized by Google

TABLE NO. VI.

SAMPLE NO. 6.—HEMLOCK BARK. (ABSOLUTELY DRY BASIS).

	Analyst	Grams extracted	Moisture %	Total solids %	Soluble solids %	Insolubles %	Nontannins: Moisture in hide %	Nontannins: Wet hide used = dry hide grms.	Nontannins: %	Tannin %	Tannin per 100 cc. solution grms.	Remarks.
1	F. Ames	35	10.80	25.72	21.28	4.44	72.96	12.70	8.38	12.90	.4028	Teas extractor (50 cc. used throughout).
3	C. R. Delaney . . .	40	9.74	27.70	24.31	3.39	76.7	11.65	9.19	15.12	.5458	Delaney Soxhlet, Journal v. 348. Sol. solid filtration 11 hours.
5	C. Fachus	30	10.80	27.35	22.53	4.82	73.64	12.65	8.62	13.91	.3724	Teas extractor.
6	J. V. R. Evans	34	10.40	27.02	*21.81	5.20	73.35	12.26	8.61	13.20	.4021	Reed extractor, modified. *Sol. solids 4½ hrs. for 50 cc.
	W. A. Fox											
7	T. A. Faust	30	10.17	26.43	22.04	4.39	73.69	12.10	8.74	13.30	.3584	Teas extractor.
8	Paul Hayes	35	10.82	27.21	21.25	5.96	73.70	12.36	8.24	13.01	.4062	Teas extractor (50 cc. used throughout).
10	F. M. Loveland . . .	40	9.95	26.22	21.74	4.48	74.27	12.86	8.04	13.70	.4935	Teas extractor.
11	J. E. McNutt	30	10.00	26.42	21.55	4.87	72.50	13.75	8.21	13.34	.3649	Teas extr'r. copper receiving flask 10 hrs. to collect sol.solids filtrate.
		30	10.00	26.36	21.38	4.98	72.50	13.75	8.01	13.37	.3609	Teas extr'r. glass receiving flask 7 hrs. to collect sol. solids filtrate.
12	T. J. Mosser	32	10.45	24.87	*20.46	4.41	73.00	12.96	8.35	12.11	.3670	Teas extractor, glass receiving flask *50 cc. evap. for sol. solids.
16	J. M. Seltzer	35	10.21	26.66	22 77	3.89	72.26	12.90	8.74	14.03	.4535	Teas extractor.

Digitized by Google

18	W. R. Snell	40	10 37	25.26	20.57	4.69	69.78	13.60	8.09	12.48	.4476	Teas extractor.
19	F. O. Sprague	35	10.44	25 61	*21.48	4.13	74.62	12.70	7.96	13.52	.4130	Teas extractor, glass receiving flask *50 cc. evap. for sol. solids.
20	G. W. Toms, Jr. . H. M. Johnquest . . Adolf Schubert . . .	25	10.44	27.48	23.08	4.40	73.30	12.55	8.93	14.15	.3171	Reed extractor.
21	W. F. Wilson[1]	25	7.50	20.71	18.18	2.53	71.20	12.96	5.73	12.45	.2879	?
22	R. H. Wisdom . . .	33	10.64	26.73	22.21	4.52	72.70	12.56	8.62	13.59	.3988	Reed extractor. "All day to get sol. solids."
	General average . . .		10.35	26.47	21.90	4.57		—	8.45	13.45	—	
Summary	Highest	—	10.82	27.70	24.31	5.96		—	9.19	15.12	—	
Summary	Lowest	—	9.74	24.87	20.46	3.39		—	7.96	12.11	—	
Summary	Greatest difference		1.08	2.83	2.85	2.57		—	1.23	3.01	—	

[1] Results omitted from average and summary.

TABLE NO. VII.

SAMPLE NO. 7.—SUMMARY OF AVERAGE ANALYSES.

		Method of cooling solution	Total Solids %	Soluble solids %	Insolubles %	Nontannins		Tannins		Grams tannin per 100 cc. by analysis
						Slow chroming %	Rapid chroming %	Slow chroming %	Rapid chroming %	
No. 1	Quebracho extract	Rapid	87.92	80.82	7.10	6.51	6.39	74.19	74.31	0.4090
		Slow	88.04	80.55	7.49	6.55	6.39	74.01	73.85	0.4074
No. 2	Chestnut extract	Rapid	42.95	42.60	0.35	14.15	14.13	28.45	28.49	0.4055
		Slow	42.93	42.58	0.35	14.18	14.17	28.40	28.43	0.4047
No. 3	Oak bark extract	Rapid	45.80	44.33	1.47	19.03	19.09	25.30	25.26	0.3916
		Slow	45.83	44.30	1.53	19.07	19.04	25.23	25.22	0.3914
No. 4	Hemlock bark extract	Rapid	50.08	46.65	3.43	20.96	21.20	25.60	25.53	0.3954
		Slow	50.03	46.78	3.25	20.92	21.15	25.87	25.58	0.3990
No. 5	Sulphite Cellulose extract	Rapid	49.98	49.90	0.07	21.01	23.67	26.73	26.11	0.3851
		Slow	49.97	49.88	0.12	22.93	23.65	26.76	26.07	0.3855

Digitized by Google

TABLE NO. VIII.

SAMPLE NO. 8.—TESTS OF KAOLIN AND HIDE POWDER.

		Tests of Kaolin		Moisture and acidity of hide powder		
		Weight of residue as per test par No. 10 grams	Reaction to phenolphthalein	Moisture in air dry hide powder %	Acidity 10 grams dry hide = cc. n/10 alkali	Method used to determine acidity
1	F. Ames	0.0014		14.80	11.80	Small's.
2	L. A. Cuthbert	0.0010	Neutral	13.00	13.00	10 gr. air dry powder + 150 cc. water in flask, phenolphthalein added and N/10 NaOH run in until the pink color remains for 20 minutes after the last addition of NaOH. The flask is vigorously shaken.
3	C. R. Delaney	0.0045	—	14.45	9.00	10 grs. shaken with 500 cc. water for one hour, filtered, aliquot part titrated with N/10 NaOH.
4	R. E. Drake	0.0006	Neutral	12.38		
5	C. Eachus	0.0007	Neutral	10.90	9.20	Hough's method.
6	Evans & Fox	0.0005	Neutral	14.90		
7	T. A. Faust	0.0006	Neutral	13.03	12.10	Hough's
8	Paul Hayes	0.0009	Neutral	14.80	12.80	Hough's
					12.30	Small's
9	A. W. Hoppenstedt	0.0005	Neutral	13.30	11.70	Hough's
10	J. E. McNutt	0.0010	Neutral	13.00	12.90	Same as No. 2.
11	F. M. Loveland	0 0015	Neutral	12.70		
12	T. J. Mosser	0.0011	Neutral	12.00	12.00	
13	M. F. Nichols			13.00	10.00	Soak 15 minutes in water and titrate with N/10 NaOH.
14	C. W. Norris	0.0003	Neutral	13.20	13.50	Hough's
15	L. M. Richeson	0.0013		14.25	12.60	Hough's
16	J. M. Seltzer	0.0006	Neutral	13.40	12.85	Hough's
17	C. C. Smoot W. G. Sprinkel	0.0014		9.25	12 80	Hough's
18	W. R. Snell	0.0006	Neutral	5.31 (?)	12.10	Digested 1 hour in 100 cc. water and titrated with N/10 NaOH.
19	F. O. Sprauge G. W. Toms, Jr.	0.0020	Neutral	11.17		
20	H. M. Johnsquest Adolf Schubert	0.0009	Neutral	13.36	11.95	Hough's
21	W. F. Wilson	0.0010	Neutral	13.60	10.40	Small's
22	R. H. Wisdom	0.0008	Neutral	13.92	13.00	Small's

Digitized by Google

There is practically no difference in insolubles or non-tannins shown in the case of chestnut, oak bark and hemlock extracts.

With the ordinary quebracho extract there is no difference in non-tannins, but the rapid cooled solutions seem to give lower soluble solids in some instances.

Ten analysts report results showing distinctly lower soluble solids by this method, one lower by the slow cooled and eleven do not vary materially one way or the other.

It might be well to consider Mr. Faust's suggestion that the solution be allowed to stand one hour before cooling in water. I think that something should be in the method in reference to agitating the solutions while cooling them in water, especially during the first part of the operation, as all of our experiments point to the fact that there is little difference between the methods if this is done, even when cooling with water considerably below 19 degrees C.

Soluble Solids.

The provision in reference to testing kaolin is a wise one. The results reported (table No. 8) show that the kaolin used in most cases answers to these tests.

Several of the collaborators remark upon the difficulty of keeping solutions within the prescribed temperature limits during filtration and also regard keeping the solutions to be filtered at 20 degrees as very troublesome, and one or two as unnecessary.

One analyst reports the temperature of the solution on the filter as rising above 25 degrees, it reaching 28 to 30 degrees. One reports 25.5 degrees in case of one sample, another 25.5 degrees and 26 degrees.

A number of analysts report filtrates as slightly opalescent, and opalescent. Some clear to transmitted light and opalescent to reflected light.

All analysts but two report funnels covered, mostly with watch glasses, to prevent evaporation during filtration, and the filtrate generally collected in narrow necked bottles or flasks; a few also report covering these with rubber rings or plates with a hole just large enough for the funnel stem to pass through.

Digitized by Google

Non-tannins.

The requirements as to washing hide powder are good, and the only comment made was to that effect.

Leaving out of consideration the results from one analyst, who evidently made no attempt to get within the requirements, the moisture in wet hide is reoprted to be from 70 to 76.3 per cent. and the equivalent weight of dry hide per 200 cc. solution to be from 11.85 gr. to 13.95 gr.

Without wishing to attach undue importance to the figures, I give the average non-tannins obtained by those analysts who used an amount of hide powder below the proposed requirements as compared with the general average.

	Non-tannins			
	Quebracho Per cent.	Chestnut Per cent.	Oak bark Per cent.	Hemlock Per cent.
Below 12.2 gr. H. P.	6.85	14.42	19.32	21.62
General average.....	6.40	14.16	19.06	21.06

The majority of collaborators were within the limits proposed, both as to moisture and weight of hide powder, and it is entirely practical to comply with the proposed requirements if it will tend to closer concordance. Mr. Hoppenstedt is not in favor of changing the limits for moisture and weight of hide from those now prescribed. Mr. Faust thinks the moisture content of wet hide should be still further narrowed—72 per cent. to 73 per cent.

Rapid Chroming (1 Hour on Shaker).

The non-tannins by this method do not differ materially, except with the sulphite cellulose extract, from those by slow chromed hide, being practically the same with chestnut, oak bark and quebracho extracts and a trifle higher with the hemlock. This method gives higher non-tannins with the cellulose extract, averaging about 0.70 per cent.

A number of analysts comment on the fact that the hide powder when chromed by this method does not absorb all the chrome from the solution.

If rapid cooling of solutions is to be allowed of course a rapid method of chroming is a necessary complement to it, but it seems to me that all the time practicable should be given to chrom-

Digitized by Google

ing the hide, or else that some such method as that used in Europe, employing a basic chrome solution, should be specified.

There seems to be some difference of opinion as to the time required to "thoroughly soak" hide powder before chroming, the time reported being from 5 minutes to 90 minutes, as follows:

5 minutes	.....	1	analyst
10 "	.....	4	"
15 "	.....	4	"
25 "	.....	1	"
30 "	.....	5	"
60 "	.....	6	"
90 "	.....	1	"

In my opinion, some specified time should be required if the rapid chroming method is to be made official and believe it would be more satisfactory if 15 minutes soaking were specified, and then chroming for 1¼ hours before shaking 1 hour.

All analysts report using No. 1F. Swedish filter paper of sufficient size to contain all the non-tannin solution, except 3 who use this paper 15 cm. diameter and 1, who used S & S No. 590.

Hide Powder.

The proposed method states that the hide powder "shall require between 12 and 13 cc. N/10 NaOH to neutralize 10 grams of the absolutely dry powder." This should read—to neutralize *the equivalent* of 10 grams, etc.

If this requirement is to be incorporated in the method, a method should be specified for determining the acidity and also, I think, directions given as to the procedure to be used to bring it to the required acidity in case it does not answer to the tests.

The results of this determination reported (table No. 8) vary from 9 cc. to 13.5 cc. I neglected to ask what hide powder was used, but think it likely that all used would test from 12.5 to 13.5 cc. by the method employed by analyst No. 2 (table No. 8).

If this be the case, it is evident that this requirement will not lead to greater concordance, but the reverse, if the individual analyst is to decide the matter, unless some uniform method is used. The moisture in air-dry hide is reported as from 9.25 per cent. to 14.90 per cent., except one much lower, which is probably wrong, or at least abnormal.

Digitized by Google

Raw and Spent Materials.

The sample of hemlock bark was sent to test this method. The analyses reported are in table No. 6. The most astonishing thing to me in reference to them is the agreement in results obtained.

Strictly speaking, there is only one analyst (No. 22) out of 15 that has fulfilled all the provisions of the proposed method in making the analysis, although No. 5 might also be admitted into that class without straining matters much.

The amount of bark taken for analysis varies from 25 to 40 grams. Nine analysts are not within the requirement as to amount of tannin per 100 cc. Five have used 50 cc. for evaporation, either for soluble solids, or for all determinations. The fact that some used 50 cc. for soluble solids determinations, and the remarks of some of those that did not have the nerve to do so, is sufficient comment on the difficulties of this determination on a solution extracted as specified in paragraph 5a.

Hemlock bark can scarcely be said to be a strange material to the American leather chemist. The following is shown in reports from the laboratories of the three members of committee submitting this method: one used 25 grams of bark and gets 0.3170 gram per 100 cc. solution, another gets 0.3584 gram and the other used 50 cc. for evaporation for all determinations.

No comments were made on the method, except as noted in table, and in reference to non-tannins being highly colored in some instances.

Temperature, Evaporation and Drying Dishes.

It may be wise to require that all solutions to be pipetted for an analysis have the same temperature, but it seems to me, that under ordinary conditions, this can make but little difference. One thing likely to influence results more would be to require the solution to be at 20 degrees when starting the determination of non-tannins.

The combined evaporator and dryer was used by all analysts reporting and the temperature during drying as follows:

Digitized by Google

	Degrees
1	95.0
1	97.0
1	97.5
6	98.0
3	98.5
4	99.0
1	99.7
1	100.0
1	100.0 about

One analyst thinks that the time for evaporation and drying should be "not less than 16 hours etc.," thus not making it imperative to remove a large number of dishes from the oven at one time. Another is of the opinion that all dishes should be 2¾ inches in diameter, not leaving any latitude in that respect.

I wish to thank those collaborating in this work and hope that the results may be of benefit to the association.

THE LEATHERSELLERS' COMPANY'S TECHNICAL COLLEGE.

We have received the prospectus for the session of 1912-13. A short history of the College is given, with description of courses and programs for the year. The catalogue contains 46 pages, with plans and illustrations showing interior and exterior views.

From 1895 to 1910 the technical school of leather manufacture under the joint auspices of the Leathersellers' Company of the City of London, the London County Council and the Borough Polytechnic Institute, was conducted at Herold's Institute, Bermondsey. During this time about 200 day students and nearly 1,000 evening students attended the courses.

The present College is housed in a new building erected by the Leathersellers' Company in 1910, and equipped with every modern appliance for the practical and scientific study of leather manufacture. Beside a full equipment for the manufacture of heavy leather, capable of working 30 hides a week, a light leather

Digitized by Google

factory with a capacity of 30 dozen skins a week, a dye house for all kinds of leather and a complete set of machines for all departments of the trade, there are laboratories of chemistry, of research and of bacteriology and microscopy, a library and a museum.

The courses in principles and methods of heavy leather manufacture are given by Dr. J. Gordon Parker, the Principal, while the corresponding work in the light leather department is done by Mr. M. C. Lamb. The chemical laboratory is under the direction of Mr. J. R. Blockley, and that of bacteriology under Dr. S. H. Browning.

THE QUALITATIVE DETECTION AND DIFFERENTIATION OF VEGETABLE TANNINS.[1]

By E. Stiasny.

In a paper published in *Collegium*[2] last year, some suggestions have been made as regards methods for distinguishing between different vegetable tannins, and preference has been given in general to precipitation and solubility tests before color tests. Since this a considerable amount of work has been done on this subject by a number of colleagues, who have been good enough to send me the results of their experiments. In collecting and publishing these results, I hope that the work which has already found the interest of so many workers, will continue until the goal we all desire is reached.

The subject may be dealt with in similar order as in the previous publication (*loc. cit.*).

A. THE LEAD ACETATE TEST.

To 5 cc. of the tannin solution (analytical strength), 5 cc. of the lead acetate (10 per cent) are added and a portion of the

[1] *Collegium*, 1912, pp. 483-499.
[2] *Collegium*, 1911, pp. 318-332, this J. vol. VI. pp. 479-496.

Digitized by Google

clear filtrate is mixed with an excess of sodium hydrate (10 per cent.; fairly fresh solution) and the formation of a yellow coloration observed. Colorless solutions are obtained with mangrove, mimosa, oakwood, chestnut, myrobalans, valonia, divi, algarobilla and gallotannic acid; quebracho and ulmo gave a slight but distinct yellowish coloration; pistacia lentiscus and sumac gave a decided yellow and wood pulp a deep yellow coloration.

The detection of wood pulp in such tannin extracts, where colorless solutions were to be expected by the above test, was therefore possible. But the fact that Quebracho gives a yellow color itself, makes the test of less value. However, for chestnut and oakwood extracts it has been found useful especially as a negative test, though the aniline test is the much more valuable one. No special remarks have been made concerning this test, by my colleagues.

B. THE ACETIC ACID—LEAD ACETATE—TEST.

Five cc. of the tannin solution (analytical strength) are mixed with 10 cc. acetic acid (10 per cent.) and 5 cc. lead acetate (10 per cent.) and the formation of a precipitate observed.

Catechol tans (quebracho, mangrove, mimosa, ulmo, gambier), give no precipitate and the turbidity produced with sulphited extracts is due to small amounts of lead sulphate. Pyrogallol tans on the other side (chestnut, oakwood, myrobalans, sumac, valonia, divi, algarobilla and gallotannic acid) give precipitates; and it must be mentioned that pistacia lentiscus behaves like a pyrogallol tan in this test. Some further information can be got by testing the filtrate of the precipitate with some drops of ferric alum (1 per cent.). The presence of quebracho, or mangrove, ulmo and gambier causes a green color (which is not always very bright and clear), while mimosa, myrobalans, sumac, divi, algarobilla and gallotannic acid give a deep buish violet. Chestnut gives a very faint violet only, while oakwood and valonia remain quite colorless. Mr. Lauffmann of the Deutsche Versuchanstalt für Lederindustrie in Freiberg confirms these observations and finds it probable that—after some more experience being obtained—a distinction between oakwood and chestnut extract may be possible by this test. In all those

Digitized by Google

cases which Mr. Lauffmann investigated, a slight violet coloration was obtained with chestnut, and a colorless solution with oakwood (compare also the table in this JOURNAL, 1911, p. 482); moreover he finds that in mixtures of oakwood and chestnut, 25 per cent. of the latter can be detected by this test.

Other applications of the acetic acid—lead acetate—test have been mentioned in the previous paper; they refer to the detection of Catechol tans in oakwood, chestnut and valonia extracts; also to the detection of myrobalans in oakwood and valonia, and (though less convincing) in chestnut extract. Catechol tans will cause a green coloration in the filtrate after adding iron alum, and Myrobalans will be detected by a distinct violet coloration.

Another remark may be made as to the different behavior of catechol tans and pyrogallol tans towards this test. There is not doubt that constitutional differences of the two groups are responsible for the solubility or insolubility of the lead compounds. But it would hardly be correct to explain these facts by the difference in the degree of acid character of the respective tannins, or by the presence of a carboxylic group in the case where the insoluble lead salt is formed. By analogy with ferric salts (see Hantzch and Desch Ann. 323 [1912] p. 1.), we may assume that the lead compounds are phenolic salts even if free carboxylic groups are present, and the fact that the lead compound of gallic acid is soluble in acetic acid shows that no conclusion as to the degree of acid character can be drawn by the solubility or insolubility of the lead compound.

C. THE FORMALDEHYDE TEST.

Fifty cc. tannin solution (analytical strength)+ 5 cc. strong hydrochloric acid+10 cc. formaldehyde (40 per cent.) boiled with reflux condenser for half an hour, cooled down very well and filtered. The appearance of a precipitate whilst boiling has to be looked for, and the filtrate is used for the following test:

Put about 10 cc. of the filtrate in a test-tube and add about 1 cc. iron alum (1 per cent.)+about 5 g. sodiumacetate (solid, without shaking); observe if blue (or violet) color appears in the lower layer.

Digitized by Google

This test is now so generally used, especially for the detection of pyrogallol tans (e. g. myrobalans) in mixtures with catechol tans (e. g. quebracho), that there seems little more to be said about it. Still there are some recent observations which have to be mentioned. While most sulphited quebracho extracts, which are on the market, behave regularly as to the formaldehyde test, there are methods of sulphiting quebracho extracts by which the extract is not so easily and not completely precipitated with formaldehyde. Dr. E. Schell has been good enough to draw my attention to this fact. If an extract is prepared in such special way as will be described below, and used for the formaldehyde test, the precipitation begins much later than with other sulphited and unsulphited extracts, and with some samples of extracts which we made on Dr. Schell's advice, 10 or 15 minutes boiling was necessary before the precipitate appeared. After 30 minutes boiling, as prescribed for the test, these special extracts are not completely precipitated, so that the filtrate of the properly cooled liquid, is more or less strongly colored. It is apparently a colloidal solution, the formaldehyde condensation produced being of different nature than in ordinary cases. We have, however, not been able by adding various substances to completely avoid this phenomenon, but there is no fear of mistaking the eventual presence of progallol tans, as the colored filtrate of these solutions gives no distinct, and at least no blue coloration after addferric alum and sodium acetate.

Quebracho extracts of such abnormal behavior have been produced by one of the following (and similar) methods:

(a) Twenty g. pure quebracho extract (liquid) was heated and 5 g. sodium bisulphite (30 per cent.) and 0.2 g. sodium carbonate in a water bath with reflux condenser for 12 hours.

(b) The extract obtained as in a) is mixed with 4.2 cc. $N/_2$ HCl.

(c) Twenty g. quebracho was treated with 5 g. sodium bisulphite (30 per cent.) and 0.75 g. sodium carbonate as described in (a).

(d) extract (c) acidified with 12.6 cc. $N/_2$ HCl.

The stronger the treatment, the more pronounced is the abnormal behavior.

Digitized by Google

Turning now to pure and untreated quebracho extracts, there is another use, which can be made of the formaldehyde test for the detection of wood pulp (and other adulterants).

Pure and untreated quebracho extracts give a very complete precipitate when treated with formaldehyde and hydrochloric acid. If this precipitate (starting from 50 cc. solution) is collected in a gooch crucible, washed (until free from chlorine), dried and weighed, the figure will amount to about 95 per cent. on the total solubles of the original tannin solution.

Presence of wood pulp will considerably diminish this percentage, though a portion of the wood pulp is coprecipitated with the quebracho. Examples:

Fifty cc. quebracho solution (corresponding to 0.2154 g. solubles) gave 0.2055 g., of formaldehyde precipitate (=95.4 per cent.).

Fifty cc. of the same quebracho solution+10 cc. wood pulp solution (corresponding to 0.086 g. solubles) gave 0.2261 g. of formaldehyde precipitate (=75 per cent. on the total solubles).

(If no co-precipitation occurred, 68 per cent. would be found.)

Fifty cc. of the above quebracho solution+20 cc. wood pulp (corresponding to 0.172 solubles) gas 0.2412 of formaldehyde precipitate (=62.3 per cent. on the total solubles; 53 per cent. calculated, if no co-precipitation occurred).

This test has been mentioned, though in the case of untreated quebracho extract there are much quicker methods of finding wood pulp.

For sulphited quebracho extracts the above test is not applicable, because the precipitate even after thoroughly washing, darkens by drying and no constant weight can be obtained. The well washed formaldehyde-precipitate besides contains considerable amounts of combined sulphur which after oxydizing with bromine can be estimated as barium sulphate, showing again that the sulphiting action on quebracho extract is a chemical one.

The quantitative estimation of catechol tans in mixtures with pyrogallol tans is not considered possible by the formaldehyde test (see also "Der Gerber" 1907) owing to the fact that considerable amounts of the pyrogallol tans are coprecipitated. The attention of those interested in this question may however be di-

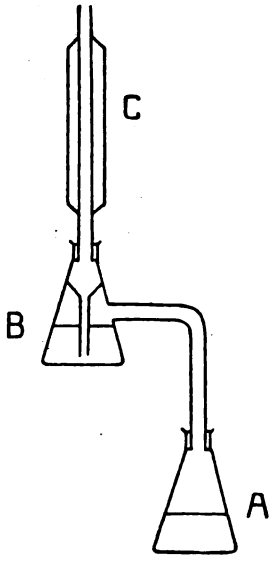
Digitized by Google

rected to a paper Small (this JOURNAL, 1911, pp. 107-111) who by a different working method obtained very satisfactory results.

D. SOLUBILITY TESTS.

Much work has been done since the last publication, on this subject, and may collaborators have contributed to our knowledge on the behavior of special tannin materials and tannin extracts to organic solvents.

As to the ethylacetate figure, the mode of procedure recommended in Coll., 1911, p. 325, was, to place 25 cc. of the tannin solution in a small separating funnel, to shake it out repeatedly with 25 cc. ethylacetate until the ethylacetate remains colorless, and to compare the dry residue of the aqueous layer with the total solubles of a corresponding volume of the original aqueous solution. Attention must be given to the fact that ethylacetate (especially when dry and pure) is considerably soluble in water,



Digitized by Google

so that it is advisable to pass a current of air for about 10 minutes through the extracted aqueous solution before taking say 20 cc. for evaporation. The dried residue must of course be subtracted from the total solubles of 20 cc. original liquid. The difference (expressed in per cent.) gives the solubility in ethylacetate. Two improvements have been made of this method; first, the use of a very simple apparatus (see figure) which allows the automatic extraction of the aqueous tannin solution. A certain amount, about 50 cc. of ethylacetate is placed in the flask A, and distilled over by means of a water bath into the flask B so that the ethylacetate condensed in C drops into the funnel and is forced to pass through the tannin solution (in B) before it runs back (through a wide side tube) into flask A. Two to three hours extraction has proved sufficient for completely extracting the tannin solution, if the ethylacetate is kept boiling so that a continuous and rapid dropping of the condensed ethylacetate is going on in the flask B. If several determinations of this kind have to be made, it simply means cleaning flask B and introducing into it a new tannin solution (25-30 cc.) when the extraction by means of the old ethylacetate in flask A can go on again.

The other improvement, which I wish to propose is the use of amylacetate in place ethylacetate. Many tests carried out by Mr. C. D. Wilkinson have shown that the solubility in amylacetate is practically the same as that in ethylacetate (see table II), amylacetate having the advantage of being insoluble in water, so that no removal of this solvent from the aqueous tannin solution is necessary.

The higher boiling point of amylacetate requires the use of an oil bath (instead of a water bath) for flask A and a cooling arrangement for flask B, which is very simply made by placing flask B in a basin with a continual stream of cold water passing through it.

The alcohol figure has been carried out as described in Coll. 1911.

Digitized by Google

TABLE I.

Tanning material or extract	Ethylacetate figure	Alcohol figure	Names of workers
Quebracho wood.....	83.3	0.0	R. Lauffmann
	74.7	—	"
	76.1	0.0	"
	74.8	0.8	"
	79.5	—	"
	76.3	0.4	"
	81.9	0.6	"
	74.4	—	L. Pollak
Quebracho extracts:			
untreated, liquid (0.5% ash)	74.5	4.6	R. Lauffmann
(0.2% ash)	77.5	4.4	"
	73.3	—	Allen and Auerbach
	72.4	—	"
	70.9	—	L. Pollak
	77.9	2.2	Stiasny and Wilkinson
	72.7	2.2	"
	80.0	0.8	"
	76.0	—	"
untreated, solid (0.3% ash).	72.9	2.1	R. Lauffmann
(0.2% ash).	75.9	0.0	"
(0.2% ash).	78.4	3.3	"
(0.4% ash).	79.9	2.0	"
	77.3	—	L. Pollak
	81.8	0.0	T. H. Davies and Hirst
sulphited .....(1.3% ash).	61.3	4.0	R. Lauffmann
(3.5% SO_2)	24.4	3.5	"
(0.8% ash).	28.4	0.0	L. Pollak
(3.5% SO_2)	2.4	3.5	"
	21.4	—	"
	27.5	0.0	T. H. Davies and Hirst
	25.7	0.0	"
(slightly).	67.6	—	Allen and Auerbach
(slightly).	64.6	—	"
	40.6	—	"
	37.4	—	"
	34.8	—	Stiasny and Wilkinson
	33.6	4.7	"
	31.1	2.1	"
	23.9	1.1	"
	18.2	—	"
	15.9	—	"
	5.6	—	"
	9.6	—	"
	23.6	—	"
treated, but not sulphited..	64.2	—	L. Pollak

Digitized by Google

TABLE I.—(*Continued*).

Tanning material or extract	Ethylacetate figure	Alcohol figure	Names of workers
Quebracho extracts	71.8	—	L. Pollak
	58.6	—	"
(0.8% ash).	65.6	5.8	R. Lauffmann
(1.0% ash).	66.4	1.1	"
(1.1% ash).	59.3	3.3	"
(0.9% ash).	65.8	3.8	"
(1.0% ash).	59.3	4.3	"
(1.0% ash).	60.7	5.3	"
Mangrove bark.....	5.2	—	L. Pollak
	11.4	—	"
	2.1	—	Allen and Auerbach
	4.0	—	"
	5.4	—	"
	6.7	—	"
	6.7	—	"
	7.5	—	"
	7.7	—	"
	8.8	—	"
	9.0	—	"
	9.3	—	"
	9.5	—	"
	9.7	—	"
	10.4	—	"
	10.5	—	"
	10.5	—	"
	13.0	—	"
	13.2	—	"
	13.6	—	"
	16.4	—	"
	34.6	—	"
	42.5	—	"
	3.9	4.9	R. Lauffmann
	2.9	4.3	"
	3.6	0.0	"
	2.1	4.7	"
Mangrove extract :			
untreated	3.4	3.8	"
	4.9	6.8	"
	0.0	1.3	Stiasny and Wilkinson
	0.9	—	Allen and Auerbach
	10.1	—	"
solid	9.7	—	L. Pollak

Digitized by Google

TABLE I.—(*Continued*).

Tanning material or extract	Ethylacetate figure	Alcohol figure	Names of workers
Mangrove Extract :			
treated and sulphited	11.4	4.6	R. Lauffmann
	11.8	9.1	"
	15.8	11.9	"
	9.1	—	Allen and Auerbach
treated, not sulphited	9.1	13.0	R. Lauffmann
	8.3	2.2	"
	12.8	8.6	"
	16.2	10.5	"
	8.5	10.8	"
	13.8	4.6	"
	14.0	5.8	"
Mimosa bark	32.5	1.6	R. Lauffmann
	42.8	0.4	"
	43.9	—	L. Pollak
	44.2	—	"
	46.5	—	Allen and Auerbach
	57.5	—	"
Mimosa extract :			
untreated	33.9	9.6	R. Lauffmann
	34.4	0.3	"
	34.2	2.3	Stiasny and Wilkinson
	37.9	0.0	"
	33.8	—	Allen and Auerbach
sulphited.....	25.6	—	"
Chestnut wood	9.2	16.9	R. Lauffmann
	4.1	11.0	"
	8.2	20.8	"
	8.5	9 6	"
	11.7	13.8	"
	17.9	—	L. Pollak
	21.8	—	"
Chestnut extract :			
untreated	14.5	19.3	R. Lauffmann
	16.0	19.8	"
	15.2	17.3	"
	12.5	13.4	"
	9.3	19.5	"
	11.8	14.3	"
	3.0	21.3	Stiasny and Wilkinson
	10.1	17.4	"
blood decolorized ..	9.4	19.1	"
South West France, " ..	10.6	—	L. Pollak

Digitized by Google

TABLE I.—(*Continued*).

Tanning material or extract	Ethylacetate figure	Alcohol figure	Names of workers
Chestnut extract :			
South France, blood decol..	9.4	—	L. Pollak
South East France, " ..	10.9	—	"
Corsica, " ..	9.6	—	"
Italy (South), " ..	9.5	—	"
	3.2	20.7	J. Chadwick
	9.8	16.9	"
	10.0	17.3	"
	9.7	16.7	Davies and Hirst
	10.3	16.1	"
	6.1	17.0	"
	6.9	17.0	"
	8.3	10.9	"
Oakwood.....	10.0	19.5	R. Lauffmann
Oakwood extract	11.2	22 8	"
	8.6	21.2	"
	12.6	21.6	"
(liquor from extraction) ...	2.0	26.7	Stiasny and Wilkinson
	20.4	32.3	Davies and Hirst
	2.0	25.9	J. Chadwick
	1.9	26.2	"
	2.1	27.1	"
treated (not sulphited).....	7.5	22.7	R. Lauffmann
slightly sulphited..... ...	11.9	26.1	"
Myrobalans :			
(fruit)	47.5	0.1	R. Lauffmann
	42.5	0.0	"
	50.5	5.2	"
	52.3	—	Davies and Hirst
	48.9	—	L. Pollack
(no stones).....	45.7	—	"
Myrobalan extract	37.3	10.2	R. Lauffmann
	37.4	14.8	"
	41.5	9.6	"
	43.1	8.0	"
	33.3	9.3	Stiasny and Wilkinson
	35.7	8.2	"
	44.4	8.2	"
	45.6	5.5	"
	39.2	—	Allen and Auerbach
	32.0	9.1	J. Chadwick
	33.0	9.8	"
	31.9	9.6	"

Digitized by Google

TABLE I.—(*Continued*).

Tanning material or extract	Ethylacetate figure	Alcohol figure	Names of workers
Valonia	7.3	24.3	R. Lauffmann
	11.8	28.9	"
	15.7	23.9	"
	8.2	26.0	Davies and Hirst
	12.8	20.0	"
Valonia extract	7.3	38.6	Stiasny and Wilkinson
	0.3	28.0	"
Trillo	58.7	—	Allen and Auerbach
Divi-divi	41.1	3.2	R. Lauffmann
	33.3	6.3	"
	36.6	9.7	"
	37.4	—	L. Pollak
Divi extract	49.7	1.8	Stiasny and Wilkinson
	38.1	—	Allen and Auerbach
Algarobilla	55.7	0.6	R. Lauffmann
Algarobilla extract	54.4	1.4	Stiasny and Wilkinson
Sumac	45.1	12.2	R. Lauffmann
	62.3	6.2	"
	59.1	—	"
	56.1	—	"
	44.2	6.6	"
	42.0	15.9	Stiasny and Wilkinson
Sumac Extract	48.5	10.2	R. Lauffmann
	51.8	7.9	"
	40.7	19.2	"
	50.7	14.8	Stiasny and Wilkinson
	56.2	10.5	"
	57.7	9.5	"
	52.3	12.7	J. Chadwick
	54.6	11.6	"
	56.2	9.9	"
Gambier	55.4	5.6	R. Lauffmann
	53.5	9.9	"
	52.3	4.7	J. Chadwick
	51.4	4.2	"
	51.6	4.2	"
Block-Gambier	64.5	4.8	Davies and Hirst
Gambier extract (Indragiri)	51.4	4.8	Stiasny and Wilkinson

In the latter case, the ethylacetate figure could be further increased (to 33.5 per cent.) by repeated treatment as described above.

Digitized by Google

TABLE II.

Tanning extract	Ethylacetate figure	Amylacetate figure
Quebracho, pure, liquid.....	76.0	77.9
Quebracho, sulphited.....	18.2	15.1
" "	15.9	11.7
" "	5.6	4.4
" "	9.6	7.8
Mangrove, pure	4.9	4.0
Mimosa, pure	34.2	31.3

Ten cc. of the solution of analytical strength are placed in a 100 cc. flask and absolute alcohol added to the mark. Fifty cc. of the filtrate are evaporated to dryness and the weight of the dried residue compared with the total solubles of a corresponding volume of the original liquor.

The figures of (Table 1) show distinctly the value of these solubility tests, the degree of accuracy of the results of different workers with different extracts of the same kind, and the influence of the treatment of the extracts, etc.

As to quebracho extracts, 23 different results (5 workers) show that untreated extracts as well as quebracho wood give an ethylacetate figure of 70-80 per cent. The few amylacetate figures obtained show the same limits. Sulphiting distinctly diminishes the solubility of quebracho extracts, and there seems to be some proportionality between the degree of sulphiting and the decrease of the solubility figure. Complete sulphiting most probably renders the quebracho tans entirely insoluble, the lowest figures obtained being 2.4 per cent. and 5.6 per cent.

It is obvious, that this behavior of sulphited quebracho extracts materially diminishes the value of the ethylacetate figure for the detection of adulterants (such as mangrove) and several attempts have been made to reconvert the sulphited extracts into original ones. This however, appeared to be impossible as the sulphiting operation is a chemical action on the tannin and it seems that this chemical action is not a reversible one. By the action of acid for instance on sulphited extracts the ethylacetate figures are but slightly increased (see Table III) and Dr. Leopold Pollak in his report, confirms this statement. A distinct though also insufficient increase of the ethylacetate figure was obtained by Dr. Pollak by evaporating 25 cc. of the analytical so-

Digitized by Google

lution on a sand bath, and extracting the dry residue in a Soxhlet with alcohol. After evaporating, dissolving the residue in 50 cc. of hot water and cooling, the ethylacetate figure was determined by the way described above and 38.8 per cent. was found in case of a slightly sulphited quebracho-extract (compared with 28.4 per cent. of the original extract). A strongly sulphited quebracho extract gave 26.1 per cent. (compared with 2.4 per cent. of the original extract).

TABLE III.

Tanning extract	Ethylacetate figure	Ethylacetate figure after acidifying
Sulphited Quebracho Extract.....	18.2	23.4
" " "	15.9	22.7
" " "	5.6	16.8
" " "	9.6	21.3
" " "	23.9	31.1
" " "	31.1	44.1

TABLE IV.

Tanning extract	Ethyl-acetate figure	Dry residue extracted in Soxhlet with Ethyl-acetate	Dry residue extracted in Soxhlet with Acetone
Quebracho, pure, liquid.....	70.9	87.4	96.1
" (Triumph), liquid.	64.2	81.2	100.0
" " " .	71.8	82.5	—
" " solid..	58.6	56.8	—
" slightly sulphited..	28.4	35.7	85.8
" strongly " ..	2.4	17.9	40.6
" sulphited, solid....	21.4	20.3	—

Dr. Pollak has also determined some solubility figures by extracting the dried solubles in the soxhlet with organic solvents; he arrived at figures (see Table IV) which in the case of ethylacetate show in most cases a distinct increase when compared with the figures obtained by shaking out the aqueous solution, but not satisfactory results are obtained with sulphited extracts and therefore the method does not promise any advantage.

As to mangrove bark, a large number of determinations of the ethylacetate figure was carried out by Messrs. Allen and Auerbach, and up to 42 per cent. of solubles were found. These surprising results can perhaps be explained by the fact that the bark of different species of trees is sold under the name of

Digitized by Google

mangrove, and that these botanical differences are responsible for the differences in the figures obtained. Untreated mangrove extracts all behave as we should expect according to the few figures published in Coll. 1911; and any treatment of the extract, either with sulphites or otherwise, seem to increase the solubility in ethylacetate (but apparently not exceeding 16 per cent.) which is quite the reverse effect to what we have seen in the case of quebracho.

In mixtures of untreated quebracho with mangrove, the ethylacetate figure will prove very valuable and it has been shown in the previous paper, and is confirmed by Mr. Lauffmann, that in such mixtures the amount of mangrove can approximately be calculated from this figure (see Table V; see also Coll. 1911, p. 327, This J., Vol. VI, p. 491).

TABLE V.

Mixture of	Ethylacetate figure	
	Found	Expected
75% Quebracho and 25% Mangrove.....	58.9	56.8
50% " " 50% "	40.5	39.0

In mixture of sulphited quebracho with mangrove, the solubility test is of no practical value for the detection of mangrove.

The figures of mimosa extract (see Table I) are in very good concordance with those given in the previous paper, and the effect of sulphiting seems to be similar to that of quebracho. The ethylacetate figure of mimosa bark is somewhat higher than that of the extract, and the difference between the figures of mimosa extracts and mimosa barks may—partially at least—be explained by the difference in the proportion of tans to non-tans and by the different solubility of tans and non-tans in ethylacetate. Besides there may be some alterations going on during the concentration of the liquors, which may be responsible for this behavior.

A considerable amount of work has been done as regards chestnut extracts, and in addition to the figures in Table I some interesting remarks have been made by Dr. Pollak, who found that the extracts of different countries are very much alike as regards their ethylacetate figures, while the trees of these countries vary in height, color of the wood, and of the liquors obtained by extraction. The average figure is 10 per cent. The

Digitized by Google

root-tannin of chestnut gives the same figure (10.2 per cent). No effect of decolorization with blood was observed, but the solubility is increased by evaporation of the liquor (see Table VI).

TABLE VI.

	Ethylacetate figure
Chestnut liquor by extraction	6.6
Same liquor after decolorizing with blood	6.3
Extract made from above liquor	10.0

Here again we find the influence of concentrating the liquor, but in the opposite direction as in the case of mimosa.

The figures obtained by Dr. Pollak, when the dry residue of a chestnut liquor is extracted in a soxhlet apparatus, were much higher, viz.: 25.9 (average of 4 samples of extract), and 20.0 (average of 3 samples of wood).

The quality of the dry wood is of distinct influence on the solubility figure obtained by extracting the wood in the soxhlet, and dark red wood (inferior quality) gives higher figures and much darker solutions than bright wood (superior quality). Some such figures (Dr. Pollak) are collected in Table VII where the solubility in acetone is also given.

TABLE VII.

Chestnut wood	% of tannin	Ethylacetate figure	Acetone figure
of superior quality (bright)	15.0%	17.9%	47.7%
of less " (dark)	14.6%	21.8%	55.3%

As regards oakwood extract, the ethylacetate figure seems to lie between 0 and 12 (one exception, showing 20.4, may be assumed to be due to adulteration until a greater number of figures are known). Anyhow, no difference between oakwood and chestnut exists, as regards solubility in ethylacetate. The alcohol figures are slightly higher (20-27), than those of chestnut (15-20).

The other figures of Table I do not want any explanation or remarks.

As regards the gelatine, iron, bromine, ammonium sulphide, and other tests, the previous publication may be referred to, as no further observations have been collected since. There are some new tests which have been proposed lately and which may be de-

Digitized by Google

scribed here though a larger number of experiments seems desirable before a conclusive judgment can be arrived at.

Bennett's test for distinguishing two groups of pyrogallol tannins. Two to three cc. of the tannin solution are mixed with 2-3 cc. sodium bisulphite (10 per cent.) and one or two drops of 10 per cent. potassium chromate. All catechol tans with this reaction, produce a greenish color. Some pyrogallol tans, viz.: myrobalans, sumac, and gallotanic acid, produce a blood red color, which rapidly fades to brown. With other pyrogallol tannins, viz.: valonia, chestnut and oakwood extracts, a deep red violet is obtained, which is pretty stable.

This test is very useful for the identification of a single tanning material; and for subdividing the pyrogalloltans into two groups; it does not, however, help to decide the frequent question of chestnut or oakwood extracts being adulterated with myrobalans.

Schell's test for detecting mangrove in quebracho extracts (natural and sulphited). Twenty cc. of the tannin solution (analytical strength; the solution must first be heated to the boiling point and then rapidly cooled, to avoid oxidation during the test) are placed in a small cylinder and immediately covered with petrol ether (to be protected from air) and mixed with 1 cc. of cobalt chloride (20 per cent.) and 1 cc. strong ammonia by means of a glass rod.

Dr. Schell states that both sulphited and unsulphited quebracho extracts give a bright greyish green coloration, while mangrove gives a brownish violet, this violet tint being easily observed in mixtures containing mangrove.

Mr. Lauffmann applied the test to other tannins and he gives his results in form of Table VIII.

Mr. Lauffmann suggests the use of this test for the identification of pure mimosa, and for the detection of algarobilla. In mixtures of quebracho and mangrove, he finds any mixed color, according to the proportion of mangrove, and the mangrove color predominating when 40-50 per cent. of mangrove is present.

Similar experiments made by the referee in conjunction with Mr. Wilkinson showed that mixtures of mangrove with quebracho extracts of different makes, gave very different colors, and that without comparing the color of the respective pure quebracho

Digitized by Google

TABLE VIII.

Tannin extract	Color produces by Schell's test
Quebracho	Bluish green
Mangrove	Lilac
Mimosa	Pigeon blue
Mallet	Bluish green
Oakwood	Green
Chestnut	Green
Myrobalans	Bright green
Sumac	Grass green
Divi	Dark green
Valonia	Dark green
Algarobilla	Bright brown
Pine bark	Olive green
Wood pulp	Green

extracts which also differ considerably from one another, it seems often difficult to come to a decision even if 10-20 per cent. of mangrove are present.

It seems therefore desirable, that a larger amount of observations be collected before a conclusive view can be arrived at.

KOHNSTEIN'S TEST (*See Collegium*, 1912, *p.* 153-158 *Abstr. This J., Aug., p.* 449.)

Mix 5 cc. of a 10 per cent. alcutin[1] solution, with 10 cc. of the tannin solution (analytical strength), filter, add a little strong ammonia to the filtrate, observe the color produced, boil and observe again the change of color.

The test is apparently a color test of non-tans, the tannin being removed by precipitating with alcutin.

The table of Kohnstein's results may be reprinted here (see Table IX).

Dr. Pollak in repeating the Kohnstein test, finds that by boiling with ammonia a precipitate is formed (this is not mentioned by Kohnstein) and that the color of this precipitate is the most characteristic feature of the test. Dr. Pollak moreover points out that the filtrate from the alcutin precipitate must be entirely clear and kaolin should be added before filtering to secure this clearness.

Dr. Pollak (See Collegium 1912, p. 234, This J., Aug., p. 449) recommends the following way of carrying out the test:

[1] Alcutin is an Albumose and can be obtained from Dr. Meyersburg, Vienna, Stumper Gasse 37.

Digitized by Google

TABLE IX.

Tanning material	Color of alcutin-pp	Color of filtrate after adding ammonia	
		cold	boiling
Quebracho	white	wine-yellow	wine-yellow
Mangrove	rose-flesh color	flesh color slightly violet	deep bordeaux red
Sumac.....	white	sulphur-yellow	orange
Knoppern	greyish white	bright flesh color	wine-yellow
Pine bark.....	reddish white	green	wine-yellow
Oak bark	yellowish	wine-yellow	bright yellow
Oakwood	brownish yellow	reddish brown	reddish brown
Chestnut	brownish yellow	reddish brown	reddish brown
Myrobalans.....	greenish white	lemon yellow	orange

Ten cc. of the tannin solution are mixed with 5 cc. of the 10 per cent. alcutin solution, a little kaolin being added and the precipitate filtered. The clear filtrate is boiled with ammonia, the precipitate which is formed, filtered through a small filter and washed with water. This precipitate according to Pollak is white (and thus escapes detection on the filter) in the case of quebracho, but reddish in the case of mangrove, and 10 per cent. of mangrove can be seen if only mangrove and quebracho are present. In extracts, which also contain myrobalans, mangrove cannot be detected by this test, as the color of the precipitate is yellowish. Mallet also gives a color similar to mangrove. The filtrate of the ammonia precipitation is, according to Pollak, more or less yellowish, both in the case of quebracho and mangrove. (See however Kohnstein's table).

The importance of the task to detect small amounts of mangrove in sulphited quebracho extracts led to some experiments made by the referee in conjunction with Mr. C. D. Wilkinson, the results of which are given in Table X.

It can be seen from this table that different quebracho extracts (all guaranteed pure) behave not quite equally, and that the presence of 20 per cent. mangrove cannot be detected with certainty in some of the mixtures, even if myrobalans are absent. Moreover, as this test merely deals with the non-tans and according to Kohnstein's view is caused by small traces of mineral salts present in the extract, there is a possibility that these mineral salts may be present by other reasons than adulteration with special tannin extracts, and thus the presence of the latter may be wrongly indicated. However, more work is desirable, by dif-

Digitized by Google

TABLE X.

Tannin extract	Color of alcutin-pp.	The filtrate boiled with ammonia
1. Quebracho, Argentine solid	yellowish brown	pp. very slightly violet filtrate yellow
2. Quebracho, pure, liquid	bright flesh color	pp. slightly colored, but not violet filtrate yellow
3. Quebracho, pure, liquid (sulphited)	bright flesh color	pp. slightly colored, but not violet filtrate reddish yellow
4. Quebracho, pure, liquid (sulphited)	bright flesh color	pp. slightly colored, but not violet filtrate reddish yellow
5. Mangrove, pure, liquid	red brown	pp. violet filtrate reddish (not deeper than in 3 and 4)
6. Mangrove, pure, liquid	red brown	pp. slightly violet filtrate reddish
7. Mangrove, pure, solid	red brown	pp. very slightly violet filtrate reddish
8. Myrobalans, pure, liquid	bright greenish brown	pp. greenish yellow filtrate yellowish brown (greenish tint)
Mixtures		
9. Quebracho (3) + 10% Mangrove (6)	bright brown	pp. very slightly violet (not distinct) filtrate reddish yellow
10. Quebracho (3) + 20% Mangrove (6)	bright brown	pp. very slightly violet (not distinct) filtrate reddish yellow
11. Quebracho (4) + 20% Mangrove (7)	yellowish brown	pp. reddish, but not violet filtrate reddish brown
12. Quebracho (4) + 20% Mangrove (7) + 20% Myrobalans (8)	yellowish brown	pp. reddish, but not violet filtrate reddish brown

Digitized by Google

ferent workers and with different extracts, before a definite conclusion can be arrived at.

Hoppenstedt's test (see this J., March, 1912, p. 170) is also a test of non-tans, but a solubility test.

Take 25 cc. of the tannin solution and add slowly, while stirring, 25 cc. of 1 cc. quinine hydrochloride, then filter. Place 5 cc. of the clear filtrate in a test-tube, add 1 cc. of concentrated acetic acid, and mix. Then add 2 cc. of acetone and mix again, then add 5 cc. of ethylacetate, mix thoroughly and shake, and then allow layers to separate. With mangrove the lower layer is colored a strongly yellow brown, whereas with all the other tannins, the layer is colorless.

In applying this test to a few quebracho and mangrove extracts, wood pulp, and mixtures of quebracho with 20 per cent. mangrove, we found that the color of the filtrate from the Quinin-precipitate is as distinct as the color of the aqueous layer finally arrived at. Further that there are pure quebracho extracts which give a definite, though faint yellow even in absence of mangrove and that there are mangrove extracts which give the test much less distinct than others, so that mixtures of quebracho with 20 per cent. mangrove may give a nearly colorless layer while other pure quebracho extracts show much more distinctly the yellowish tint. Wood pulp, by the way, gives also a yellowish shade.

TABLE XI.

	Tannin extract	Color of the lower layer (Hoppenstedt test
1.	Quebracho, solid	colorless
2.	" liquid, pure	slightly, but distinctly yellowish
3.	" sulphited	colorless
4.	" sulphited	colorless
5.	Mangrove liquid	strongly yellow
6.	" liquid	yellow
7.	" solid	strongly yellow
8.	Wood pulp	slightly yellow
9.	Quebracho (3) + 20% mangrove (6)	very slightly yellow (less distinct than [2])

Table XI gives the results obtained by the referee and Mr. Wilkinson. We should like other colleagues to communicate their experience with the Hoppenstedt test before coming to a conclusion as to its value.

Concluding this report, we may say, that there seems to be some resemblance between the qualitative analysis of tannins

Digitized by Google

and that of oils, as in both cases a number of figures and tests are necessary to allow a conclusion, which in some cases is not very easy. Of those tests which hitherto have proved of greatest value in this respect, we may mention the solubility tests, the formaldehyde test, the acetic acid—lead acetate test, the anilin-test and the bromine test, but many more tests (see previous paper) ought to be made and the amount of tans and non-tans and their proportion considered, the Löwenthal figure determined, etc. In some cases the dyeing of cotton strips will also prove useful.[1]

ABSTRACTS.

Importance of Chemical Control in the Leather Industries. M. S. SALAMON and W. M. SEABER. *Leather Trades' Review*, Vol. 45, pp. 33-4, 116-7, 195-6, 348-9. *Washing and Soaking.*—High temporary hardness is likely to cause trouble, due to precipitation of carbonate of lime on the pelt, causing hard spots and uneven tannage. Uneven dyeing also results from deposits of chalk in the leather. In the fat-liquoring process, the soap used is decomposed by calcium and magnesium carbonates in the leather, forming insoluble soaps. Hard waters may be improved by the addition of caustic soda (not to exceed 0.1 per cent.). *Unhairing.*—Lime may contain many impurities, as silica, magnesia, iron, alumina, and calcium carbonate due to incomplete burning. It is desirable to know the composition, not so much because of injury which the impurities may cause as in order to prevent lack of uniformity in the action of the limes due to variation in the different consignments. Lime should not contain iron oxide. The author mentions a sample containing 4 per cent. Fe_2O_3. Sulphides of lime, soda and arsenic are now often used with lime to hasten the process of unhairing. Sodium sulphide should be free from carbonate, and from iron. Arsenic sulphide may contain sulphur or arsenious oxide, neither of which is of any value. It is important to know the degree of purity of both arsenic and sodium sulphides. "Tank waste" from the Leblanc soda process, containing calcium sulphide is also used, and it is important to know its composition.

Deliming, Bating, etc.—The action of dung bates is so little understood that not much can be done in the way of chemical control. Acids used for deliming must be tested for strength and purity. Formulas for several deliming and drenching processes are given. *Tanning Materials.*—Any valuation of a tanning material must be based chiefly on its tannin content, though some forms of adulteration with cheaper tannins can be detected. One of the important services rendered by the chemist is in the examination of spent materials, which should not contain more than

[1] Specially recommended in Mr. Lauffmann's report.

Digitized by Google

1 per cent. of tannin. In examining spent liquors, an important point is the proportion of acid. Too little acid permits the hides to shrink from the astringent action of the tannin. In the case of sole leather, thorough preliminary deliming is not necessary if the acidity of the liquors is kept up, but if it is not, the lime remaining in the hides may react with the tanning materials to produce stains. *Alum Tannage.*—Alum is liable to contain iron, which may be detected by boiling its solution with a few drops of nitric acid and adding potassium ferrocyanide solution. A blue color indicates iron. Free sulphuric acid may be detected in aluminum sulphate by adding logwood solution, giving violet if the salt is neutral, but brown-yellow if it is acid. The acidity may be corrected by allowing the solution to stand for some time after adding some granulated zinc.

Chrome Tannage.—The main sources of chrome for tannage are the bichromates of soda and potash. The percentage of chrome in these should be determined. In the two-bath process, the bichromate should be in excess in the first bath. When the first pack has been removed, the amount of bichromate in the spent liquor is determined, and enough bichromate is added to replace what has been used up, and a full dose of acid. (Neither here nor under spent vegetable tan liquors does the author make any allusion to the effect of the accumulation of salts of soda and potash in the liquors.—Ed.) In the one-bath process the basicity of the liquor should be known. In both processes, the acid remaining in the leather must be neutralized, and care must be taken to avoid over-neutralization. Borax or bicarbonate of soda solution is often employed. Hypo used in the second bath must be tested for available SO_2. Hydrochloric acid must be tested for strength and impurities, especially sulphuric acid.

Oils and Fats.—The tanner is obliged to be on the lookout for adulteration in the oils and fats used in his work. Tallow is often adulterated with cottonseed oil, stearin, resin, or paraffin. Some of these may be detected by smell. Good tallow is almost odorless. Neats-foot oil is subject to all sorts of adulteration, bone oil, cottonseed oil, lard oil and mineral oil being often met with. Neats-foot should not deposit much stearin on cooling. Tallow oil is a good substitute for neats-foot. Olive oil is used in making some kinds of fat-liquors. The amount of fatty acids due to rancidity should not be high. A small proportion is an advantage, as they aid the formation of emulsions. Sesame, rape and cottonseed oil are adulterants. Castor oil is often adulterated with rosin oil. Turkey red oil (sulphated castor) is a soluble oil, and if pure gives a clear solution in water. Linseed oil is tested by coating glass plates 3 by 4 inches in size with a thin film and exposing to air and light, noting when the film ceases to be "tacky." A good oil should dry in 3 days. In comparing different samples they should be run at the same time, as differences in atmospheric conditions influence results largely. Ash of linseed oil should be very small. Cod oil is often adulterated with mineral or rosin oils or with other fish oils. Cod should not be high in

Digitized by Google

acid, as this increases the tendency to spue. Degras and sod oil should not contain an excess of either acid or alkali, no iron and not much water.

Beeswax is extensively adulterated, often with Japan wax, carnauba, paraffin and rosin. The last is particularly undesirable because of its tendency to oxidize and discolor after bleaching. Soaps should be tested for excess moisture and for silicate of soda.

Dyeing troubles are often traceable to the water used. Hard water may be made to work well by the addition of sodium bisulphate or, for basic dyes, of acetic acid. Waters containing alkaline carbonates should be carefully neutralized with acid. The best tests of dyes are actual experiments on small samples of leather.

Effluents should be examined (1) to prevent loss of valuable materials, (2) as a check on the working of the tannery processes, and (3) to prevent the contamination of streams. Coal should be tested for calorific value. Periodical control of all products and liquors is just as important as the annual stock-taking.

The Acidity of Tannery Liquors. HUGH GARNER BENNETT. *Leather Trades Review*, Vol. 45, pp. 266-9 and 342-4. This paper includes the same material as that abstracted in the July issue (pp. 382-5), with additions. The writer's comments on existing methods were pretty fully given in the former abstract and will not be repeated here. Bennett tried various other methods with unsatisfactory results, of which he gives a summary. (a) Detannization with copper acetate was incomplete even after standing and heating. (b) Detannization with hide-powder removed much acid. (c) Attempts were made to extract the acid with immiscible solvents. Many were tried without success. Only ether, chloroform and benzene are mentioned. (d) By measuring the amounts of SO_2 given off by the action of the liquor on sodium sulphite. The method resembles that of Phelan and Fiske (this J., Vol. 3, p. 99). Results were neither accurate nor concordant, and tannin was included. (e) Distillation in steam was tried as a means of determining the volatile acid. Twenty-five cc. of a 25° Bk. liquor was distilled in steam. The distillate collected in portions at intervals and titrated. Acid continued to come over at a slowly diminishing rate for a long period. In some instances the total acid found was three times that indicated by the lime water test. The author explains this by supposing acetate of lime in the liquor to have been decomposed by hydrolysis.

The important thing is to differentiate plumping acids from those which do not plump. Plumping power depends, among other things, on, (1) "The concentration of the acids which really plump, *i. e.*, the actual amount per cent. (2) The nature of the anion of these acids. (3) Their strength, *i. e.*, the amount of their ionization. This is influenced not merely by their nature and their concentration, but by other factors, such as the presence of neutral, *e. g.*, lime salts, which last, in turn, depend upon the quantity of goods working forward, the quantity of lime in those

Digitized by Google

goods, etc. These may be considered the positive factors, while the negative factors are, (4) The concentration of tannin present, *i. e.*, the amount per cent. (5) The nature of this tannin, mild or astringent, mellow or sharp. Gambier, for example, may be said to plump negatively, *i. e.*, it is so mellow that it gives the true plumping acids the best chance. (6) The ionization of the tannin may be a factor; its effect, however, is as yet obscure."

Procter's work on gelatin illustrates the difficulty of estimating the plumping power of a liquor. The additional complications in the case of hide in the presence of tannin are so great as to render the problem apparently hopeless. The nearest approach that has yet been made to a formula for plumping power is the ratio of plumping acids to contracting acids.

To compare the lead-oxide method with others, five liquors from the same tanyard, ranging from 108° to 48° Bk. were analyzed, and then diluted so that each contained 0.4 per cent. tannin, and the acidity determined by several methods with the following results, which are in cc. N/10 soda per 10 cc. of diluted liquor.

No.	Original tannin percentage	Direct titration phenolph.	Gelatin method	Lime water method	Lead oxide method	Direct titration methyl or.
1	16.2	1.9	1.1	0.9	0.2	0.45
2	12.2	2.6	1.6	1.1	0.35	0.45
3	8.6	3.3	2.0	1.5	0.55	0.35
4	3.7	4.3	2.9	1.8	1.1	0.2
5	1.8	6.5	4.8	2.7	2.5	0.0

The direct titration was done by spotting out on test paper. The results obtained with methyl-orange are due to the increasing amounts of lime salts in the older liquors. The liquors contain three types of acid, the tannin type, the gallic acid type and the acetic acid type. Phenolphthalein being sensitive to all these acids, shows the largest total. The gelatin method also uses phenolphthalein as indicator. The tannin being removed, results are lower. Higher amounts of acid of the acetic type involve larger loss in precipitating the tannin, hence the differences are not constant. Lime water estimates the gallic acid incompletely. The lead oxide method throws out both tannin and acids of the gallic type, hence giving low results. Calculating these results into acidity of the original liquor gives the following, in which the number of cc. N/10 soda equivalent to 10 cc. of the original liquor is given in each case.

Liquor No.	Direct titration phenolph.	Gelatin method	Lime water method	Lead oxide method
1	77.0	44.7	36.6	8.1
2	79.0	48.7	33.6	10.7
3	71.0	43.0	32.2	11.8
4	40.0	26.8	16.6	10.2
5	29.0	21.6	12.2	9.9

Digitized by Google

The acidity shown by the lead oxide method increases at first as the liquors are sapped, and afterward diminishes. The author regards this as representing correctly the state of affairs, the acids at first increasing as the result of fermentation, and later diminishing because of absorption by the hide.

The gelatin method also shows an increase of acid at first as the liquors begin to sap, and afterward a diminution. The author regards gallic acid as the predominant influence here, the amount increasing at first because of decomposition of tannin, and afterward decreasing because it is absorbed by the hide.

Emory Oak. The Forest Service has published a bulletin on this oak, which will grow in the semi-arid regions of the southwestern part of the United States. Beside its value for lumber and fire-wood it promises to be a source of tanning material. The bark shows 16.1 per cent. total solids, 14 per cent. soluble solids, 2.1 per cent. reds, 6.6 per cent. nontans, 7.4 per cent. tannin. The wood gives total solids 8.3 per cent., soluble solids 7.5 per cent., nontans 4.4 per cent. and tannin 3.1 per cent. The color of the tannin is rather dark.

Salt Stains. A. Jouve. *La Halle aux Cuirs*, August 11, **1912.** The antiseptic action of salt is insufficient to prevent the growth of putrefying bacteria. Acid-forming bacteria also grow in the presence of salt, causing changes in the hide wherever fermentation goes on. Three causes of stains are assigned: (1) Liquefying bacteria. These are rather large, and are raised on the untanned skin. In process of tannage they become depressed and take a color different from the rest of the skin. (2) Iron. (3) Stains of the third sort are due to acid swelling provoked by magnesium chloride present in the salt. They are important in proportion to the quantity of $MgCl_2$ present. Pure salt, neutral or slightly alkaline, produces no stains, and prevents acid fermentation. With rock salt, some stains were produced. The use of sea salt was always followed by the formation of stains. If, however, sea salt be neutralized or rendered alkaline, the stains are prevented. $MgCl_2$ causes insolubilization of the hide, without hindering the penetration of tannin. The hide substance causes a partial dissociation of $MgCl_2$, bringing about a sort of magnesia tannage and liberating HCl which causes swelling and partial solution of the adjacent hide.

The author suggests (1) that the bacterial action be prevented by antiseptics, and (2) that $MgCl_2$ be destroyed by soda, converting it into $MgCO_3$. The excess of soda would be harmful. $BaCO_3$ may be used, as both it and the two products of its reaction with $MgCl_2$, $BaCl_2$ and $MgCO_3$, do not act on hide. L. B.

Causes of Salt Stains and Means of Avoiding Them. Dr. Rappin, T. Grosseron and L. Soubranne. *La Halle aux Cuirs*, July 28, **1912.** Hides

Digitized by Google

are cured chiefly by drying or salting or a combination of the two processes. The first is objectionable because the dry hides are liable to convey disease germs, especially anthrax. The careless manner in which salting is commonly done permits the flesh side of the hide to become infected with bacteria, some of which can grow in the presence of salt. Three kinds of causes contribute to the formation of salt stains, chemical, physical and bacterial. Of the first, the substances used in denaturing salt are important. Physical causes include sudden changes of temperature. Microbes live and multiply in the hair-follicles, and these often become centers of decay. Nine samples of crude salt examined contained from 6,000 to 76,000 bacteria per gram, and from none to 700 mold spores. Salt is often used again and again, becoming very badly contaminated with microörganisms as well as filth. The authors have isolated several organisms including a streptothrix, whose role in the formation of stains they hope to establish. They recommend that sterile salt be used, and means used to prevent adding to the number of bacteria present on the freshly flayed hide. L. B.

Formaldehyde Tannage. L. MEUNIER. *Collegium*, No. 508, p. 420-4. In 1898 Payne and Pullman were granted a British patent for formaldehyde tannage in which they used potassium or sodium carbonate or other feeble alkali. Griffith in the *Leather Trades Review* (1908) stated that certain mineral salts in acid medium, notably alum and sodium bisulphite, could be used with formaldehyde with excellent practical results. It is thus apparent that the alkaline carbonates do not act as alkalies in formaldehyde tannage. Meunier and Seyewetz have shown (Abstr. this J., VII, p. 230) that a concentrated solution of K_2CO_3 by dehydrating skin produces a sort of tannage. By the following experiment Meunier shows that it is the dehydrating effect of K_2CO_3 which is essential in the case of formaldehyde tannage. Five pieces of goat skin were suspended in solution of K_2CO_3 containing 800, 400, 100, 50 and 20 grams per liter, and one in pure water. Six other pieces were similarly treated except that each solution contained 0.3 per cent. of formaldehyde. After 5 hours the pieces were pressed between filter papers without washing, and dried. Those from the strongest solutions of K_2CO_3 dried at once, and were to all appearances white pliable leather, fibers quite separated. Those from the 40 per cent. solutions were similar to these; those from the 10 per cent. solutions somewhat pliable, while all the rest, drying more slowly as the percentage of K_2CO_3 diminished, were quite stiff and horny. All the pieces were now thoroughly washed and again dried. The pieces which had been treated with 0.3 per cent. formaldehyde were not altered by washing, while the others were all reduced to the same horny condition. Dr. Meunier thus sums up his conclusions: There are two actions in formaldehyde tannage; first, isolation of the fibers by dehydration due to the mineral salt present; second, fixing of the fibers in this condition by the tanning action of formaldehyde, thus rendering them immune from the action of cold water. L. B.

Digitized by Google

Tannage by Means of Salts of Cerium. F. GARELLI. *Collegium,* No. 508, pp. 418-20. The author takes exception to W. Eitner's statement (*Gerber,* Aug. 1 and 15, 1911, and *Collegium,* 490, Dec. 16, 1911) that solutions of normal cerium chloride ($CeCl_3$) convert hide into a material more like rubber than leather. Garelli had the same experience when the solutions were too acid or too concentrated. When nearly neutral and sufficiently dilute these solutions tan as well as the salts of aluminum. The leather is pliable, white, elastic, of full "feel" and beautiful grain, similar to that produced by solutions of ceric chloride ($CeCl_4$) or nitrate. The ash of the leather was 10.6 per cent., of which 9 per cent. was Ce_2O_3. L. B.

The Various Methods of Preparing Artificial Leathers. HANS SICHLING. *Collegium,* No. 508, August, 1912, pp. 334-347. The author distinguishes two classes of leather substitutes, the first using ground-up leather as a basis, the other substituting vegetable fiber. The bulk of the article consists of a catalogue of processes which have been patented. L. B.

The Dyeing of Leathers. A. CHAPLET. *Le Chemiste,* Vol. III, No. 2, p. 21. A brief resumé of methods and materials for the various kinds of leather. L. B.

The Theory of Tannage. B. KOHNSTEIN. *Oesterreiche Chem. Ztg.,* 1911, p. 73, through *Moniteur Scientifique.* The laws which apply in the absorption of tanning solutions by hide-powder or colloid solutions do not hold in the case of animal membrane. Dr. Neuner has shown that in some respects the behavior of skins toward tanning agents is exactly opposite to that of hide powder. Tannage is a chemical process, whether produced by vegetable tannins, by mineral salts or by oils. According to Nierenstein and Fahrion the process is one of condensation. Fahrion considers that the tannin furnishes oxygen, the basic groups of the hide furnish hydrogen, and that thus water is formed and splits off. It is true that tanning solutions are colloidal, that the hide is a gel capable of swelling, that the fixation of the tannin takes place by absorption, and under the action of capillary forces, but a chemical action is connected with these physical processes. The chemical theory of tannage is supported by the fact that if decay has begun in a hide, the decayed parts will not tan. It has been generally held that formaldehyde tannage is purely chemical. The author thinks this is not the case, and classes formaldehyde tannage with that produced by alcohol, since formaldehyde leather when heated to 140° C. in an autoclave cannot be distinguished from untanned hide which has been similarly treated. L. B.

Decolorization and Carification of Tanning Extracts. B. KOHNSTEIN. *Oesterreichische Chemiker-Zeitung,* No. 1191, pp. 70-73, through *Moniteur Scientifique,* June, 1912, pp. 385-9. Means used to clarify and decolorize tanning extracts include cooling, filtration, the addition of chemicals or

Digitized by Google

bodies having the power to absorb coloring matters very energetically, and the protection of the extracts from the action of air and light. In extracting mangrove by means of a battery of autoclaves, the leaching may be well done, the color is improved because of protection from air and light, and the liquor is partially clarified by filtration in flowing through the material of the sevreal autoclaves in succession. As the liquor flows along through the series its temperature falls, and this fact aids in the clarification, since cooling precipitates some of the coloring matter and gummy material. L. B.

Tanning Hides with the Hair on. *Gerber-Courier,* Vol. 53, No. 31. For green hides which do not require much softening usually 12-24 hours' soaking in fresh water will cleanse them from blood, dirt, etc., and make them thoroughly soft. For softening dried hides borax is very appropriate. Five to six pounds dissolved in warm water will suffice for 1,000 gallons of water and the efficiency may be increased by raising the temperature with steam to about 90° F. (32° C.). After about 12 hours in this soak the hides must be worked on the beam, drummed or milled in some manner. For further softening the hides are placed in a decidedly salty liquor and soaked for 12-24 hours after which they are drummed for a half hour in a drum arranged with wooden pins and replaced in the soak for another 12 hours. After this soaking the hides may be fleshed. A common process for tanning or preserving hides of this sort is to use alum and salt. Hides so tanned, however, become moist and heavy in damp weather owing to the absorption of moisture. After fleshing and trimming the hides are laid in a pretty strong solution of alum and salt, care being taken to expose the flesh side thoroughly to the liquor and to give the hides plenty of room so as to permit occasional raising. Six pounds of alum and 12 pounds of salt are used to every 100 pounds of hide. The hides must remain long enough in the liquor to permit thorough penetration and afterwards are withdrawn, allowed to drain and hung up to dry. When they are about two-thirds dry they are laid in piles for a few days to become soft and damp to the same degree throughout before they are dressed to the required thickness. This requires special care as in warm weather especially the heat developed often causes injury. The dressing to the required thickness is usually done by hand and requires considerable ability and insight. The hides can then receive an after-tannage to considerable advantage.

Several methods can be used for after-tannage, viz., alum and salt liquors either in a vat or pin-drum; aluminum sulphate and salt followed by treatment with hyposulphite of sodium; gambier and salt in a pin-drum; or a combination of quebracho and hemlock liquors or quebracho liquor alone. The treatment with aluminum sulphate and salt is very good. About 4 pounds of sulphate and 8 pounds of salt are dissolved in 20 gallons of water for every 100 pounds of hide. In this solution the hides are drummed for from ½ hour to 1 hour, then about 10 pounds

Digitized by Google

hyposulphite of sodium dissolved in 5 gallons of warm water to every 100 pounds of hide are added and a further drumming for half an hour is sufficient. By this treatment the tanning material is combined firmly with the hide-fiber and cannot be washed off by water. When taken from the drum the hides are rinsed with cold water, allowed to drain and hung up to dry. After drying an oil or fat dubbing is applied to restore the softness lost during the drying and the hides are scoured with sawdust. By the use of gambier and salt the hide is made soft and strong permanently. Gambier tannage can be done in a vat or drum and is continued until the liquor has penetrated the hide thoroughly. The hides are then allowed to lie in a pile for 48 hours to drip off well and are hung up to dry. To obtain softness, oils, mixtures of oil soap and tallow, fish oils, and mineral oils of good quality all give good results. The oil is applied on the flesh side and allowed to penetrate slowly; the hides being piled and allowed to remain thus for some time. The slower the drying the softer the finished product. The finishing is best carried out in specially built revolving drums and must be repeated two or three times to obtain a product thoroughly soft and clean. Calf skins and other hair skins may be tanned in the manner recommended for hides. In the alum tanned skins, yellow ochre added to the sawdust used for scouring gives a yellow color to the flesh side. L. A. C.

Report of the Analysis Commission of the German Section. PROF. DR. PAESSLER. *Collegium*, 1912, pp. 182-7. The subject investigated was the determination of sugars in extracts, using von Schroeder's modified Fehling's method; after complete removal of the tannin, the reduction is carried out and the cuprous oxide finally reduced to metallic copper and weighed. For cane sugar a portion of the tannin freed solution is inverted by boiling with acids. For details reference is made to Heft VI of Paessler's "Die Untersuchungsverfahren des lohgaren und des chromgaren Leders und die Zuckerbestimmung in Gerbemitteln, Gerbstoffauszügen und Gerbebrühen." Four samples of extracts and a special sugar solution (5) were used for the comparative analyses which were carried out by six chemists. The German Tanning School was represented by Herr Appelius and the Freiberg Research Institute by Herr Laufmann. The averages are shown in the table:

	1 Chestnut extract		2 Oakwood Extract		3 Quebracho ext. pure		4 Quebracho ext. sulphited		5 Sol. tannin grape and cane sugar	
	Grape	Cane	Grape	Cane	Grape	Cane	Grape	Cane	Grape	Cane
Dr. Besson	5.2	1.2	3.9	1.5	0.2	0.3	0.6	0.2	3.2	2.2
Gerberschule	5.5	2.5	4.0	1.9	0.4	0.2	0.7	0.2	3.0	2.5
Versuchsanstalt	5.5	2.3	3.9	1.9	0.3	0.3	0.2	0.3	3.4	2.2
Dr. Fritz Moll	5.8	1.6	4.4	1.8	0.9	0.4	1.1	0.5	3.0	2.3
Prof. Dr. Philip	5.1	2.9	3.7	1.8	0.2	0.6	0.1	0.6	2.6	2.2
Dr. Sichling	5.3	2.9	4.1	2.0	—	—	0.5	—	—	—

Digitized by Google

The closest agreement is with grape sugar in chestnut and oak and with both sugars in the artificial solution; the greatest discrepancy is with cane sugar in all extracts and grape sugar in quebracho. The chairman conjectures that the cause of these variations lies in slight deviations in the details which require here to be closely followed. Before reduction it is absolutely essential that the solution be free from tannin and lead salt, repeating the treatment with more basic lead acetate or sod. sulphate as needed. It is suggested that this work be repeated with more painstaking adherence to the details. The sample should be examined immediately before decomposition sets in. Dr. Besson reports that in the case of extract No. 1, in order to obtain a ppt. suitable for filtration in Allihn tubes, he could only use 10 gms., diluting to 500 cc. and employing 25 resp. 50 cc. for the Fehling's reduction. After it had been found that the amounts of copper obtained by reduction were practically equal, he weighed the cuprous oxide directly in the remaining determinations. The chairman admits this is a simplification, but would not recommend it since at times small amounts of organic matter may be carried down which should be burned off before weighing.

For the Freiberg Institute experiments have been made upon the influence of time on inversion. The percentages of cane sugar found in the above extracts were:

	(1)	(2)	(3)	(4)	(5)
4 hours inversion....	3.1	2.2	0.4	0.3	2.2
½ hour inversion....	2.3	1.9	0.3	0.3	2.2

This shows that prolonging the inversion in the case of chestnut and oak extracts, the quantity of cane sugar is increased. The prescribed length of time should therefore be rigidly adhered to. The influence of the strength of acid was tested upon the oak extract, giving the following percentages of cane sugar:

Dilution of H_2SO_4.....	1:6	1:5	1:4	1:3
Cane sugar found.....	1.45	1.85	1.95	2.15

This also shows that a standard strength (1:6 prescribed) should be strictly followed. W. J. K.

The Salting of Hides. A. A. Besson. *Collegium*, 1912, 187-197. At a recent congress of French leather merchants, during the discussion of salt spots the opinion was advanced that the denatured salt of the East was impregnated with iron and that on this account sea salt had to be used instead. The author therefore examined various salts and found that on the contrary, sea salt contained much more iron than that from the brine wells (salines); further the iron present is mostly insoluble and the amount reaching the hides is very small. Even if all dissolved, the amount would be only 0.12 gm. per square meter. His view is that the character of the salt employed has very little to do with the stains and that the cause must be sought elsewhere. He quotes a circular of questions which he had sent out to the principal French salters and sum-

Digitized by Google

marizes the replies. These vary considerably but agree in reporting the salt spots as worse in summer cured hides. A letter from M. Loulier of Rennes is reprinted entire; this salter who in 16 years' practice has had no complaint of salt stains in his calf skins, proceeds as follows. After the hides are cold, that is at least several hours after slaughter and according to weather (for in the warm season it is necessary to avoid overheating or decomposition which is manifest by odor and looseness of hair), they are spread flat and 1,000-1,200 gms. sea salt applied evenly to the flesh of each. To prevent direct contact of salt with the delicate grain, the hides are piled in pairs, flesh to flesh, with the larger hide beneath.

The writer believes that the antiseptic power of salt is insufficient in warm weather to prevent the spot formation which is primarily due to microbic action. The improved results obtained with borax demonstrate this. Among other experiments, the author has found that the ash of the spotted hide contains less iron than that of the clear hide; this is because the amount of ash (after deducting salt) is greater in these parts.

Selected from the analytical tables:

		Salt	
	Souble $FeCl_3$	Soluble $FeCl_3$	insoluble $FeCl_3$
Brine No. 1, France.....	0.0006	0.0012	0.0029
Brine No. 2, France.....	0.0030	0.0006	0.0009
Brine No. 3, France.....	0.0006	0.0012	0.0029
Salt, Baden	——	0.0006	0.0020
Salt, Hanover	——	0.0006	0.0026
Seal Salt	——	0.0006	0.0104

Since the brine yields about ⅓ its weight of salt, the figures show good work. W. J. K.

Constitution of Tannin. M. NIERENSTEIN. *Annalen der Chemie* [388], 223. Earlier investigations have shown that tannin leviss. puriss. Schering consists essentially of digallic acid $(OH)_3C_6H_2.CO.O(OH)_2.C_6H_2.COOH$ and leucodigallic acid[1] $(OH)_3C_6H_2.CH(OH).O.(OH)_2.C_6H_2.COOH$. From the products obtained by acetylization together with measurements of optical activity a content of 18.5 to 22.7 per cent. of leucodigallic acid is computed; since this has no tannoidal power, *i. e.*, is not fixed by casein or hide powder, while tannin contains almost 100 per cent. tans, this last must contain the leucodigallic acid as a component of the molecule and not in mixture. On the basis of the observed high molecular weight of tannin and his own experiments (below), the author proposes as the simplest formula

$$\begin{array}{l} (OH)_3.C_6H_2.CO.O.(OH) \\ \qquad\qquad .C_6H_2.CO.O.(OH)_2.C_6H_2.CH(OH).O.(OH)_2.C_6H_2 \\ \qquad\qquad\quad | \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad | \\ \qquad\qquad\quad O \text{ ———————————————— } CO \end{array}$$

[1] Formerly called leucotannin, which name is now discarded.

Digitized by Google

digalloylleucodigallic anhydride. For this the ratio digallic acid to leucodigallic acid is 1:1 but the various tannins contain more complex ratios, 2:1, 3:1, etc. The tannins here examined are classed as tri- or tetradigalloylleucodigallic anhydride.

Leucodigallic Acid.—The author had previously isolated only acetyl derivatives. He now has obtained the free acid.

1. Reduction of Tannin: Iljin's method was used; 100 gms. tannin were heated with 100 cc. H_2O, 100 gms. Zn dust for 24 hours. The resulting ppt. was decomposed with H_2SO_4 and the solution obtained extracted with ether whereby three layers separated. The upper etherial layer yielded (as Iljin found) gallic acid and the author also found gallic anhydride. The middle layer on extraction with ethyl acetate gave mixed crystals of d- and dl-leucodigallic acids which could not be fractionated.[1] The ratio amounts were 1:6 and the total yield was only 5.6 gms.

2. Reduction of Digallic Acid: One gram digallic acid was similarly reduced with zinc and yielded gallic acid and racemic leucodigallic acid. A better yield (89 per cent.) was obtained by reducing with calcium hydride. dl-Leucodigallic acid crystallizes from alcohol and chloroform in fine needles of m.p. 278-80°. A quantitative tanstuff determination gave 99.4 per cent. non-tans which distinguishes it from digallic acid which yields 99.6 per cent. tans.

3. Derivatives: Acetylization of the leucodigallic acid with acetic anhydride yielded pentaacetylleucodigallic acid $(CH_3CO.O)_3.C_6H_2.CHOH.O.C_6H_2.COOH(O.COCH_3)_2$, m. p. 172-3° while acetyl chloride gave the hexaacetyl derivative, m. p. 155-6°. On treatment of leucodigallic acid in alkaline solution with ethylchloroformate, hexacarbethoxyleucodigallic acid

$$(C_2H_5.O.CO.O)_3—C_6H_2—CH(O.CO.OC_2H_5)—O.C_6H_2.COOH(O.CO.OC_2H_5)_2,$$

m. p. 123°, was obtained.

4. Separation of the Racemic Components: This succeeds best with the strychnine salts of the carbethoxy compound above, the laevo salt crystallizing out first. The acids thus separated were decarbonated by heating with dilute pyridin, yielding the two optical modifications. l-Leucodigallic acid melts at 276-7°, gives a red color with KCN and does not ppt. gelatin; its rotatory power diminishes with time. The d-leucodigallic acid likewise melts at 276-7°, and is identical with the acid obtained by reduction of tannin.

5. Reactions of Leucodigallic Acid: On oxidation with hydrogen peroxide, ellagic and puteoic acids are formed; with potass. persulphate, purpureo tannin is yielded. (JOURNAL [6], 359.)

The author (with others) has earlier shown that the condensation product of formaldehyde with phenols in presence of HCl consists of 100 per cent. water insoluble diphenylmethane derivatives, while aromatic acids yield also (or only) soluble oxyaurin acids. Applied to tannin, etc.,

[1] Under the microscope two forms of crystal could be separated mechanically.

Digitized by Google

this reaction shows digallic acid to resemble gallic acid, while leucodigallic acid behaves like tannin and perhaps as a component of tannin gives it this property.

	Per cent. insoluble diphenyl-methane derivatives	Per cent. soluble oxyaurin-carbonic acids
Gallic acid	74	26
Tannin	0	100
Digallic acid	80	20
Leucodigallic acid	5	95

(Condensed.)

The Tannin Molecule.—Preparation of Pure Tannin: This problem is as yet unsolved. The author has analyzed preparations containing from 50.2 to 54.5 per cent. C which is about the range of published results by various observers. He does not regard tannin nearly so hygroscopic as Iljin states (ante, p. 131) and attributes the variations to accidental irregularities in mixtures. The author has purified tannin by solution in ether and gradually precipitating with chloroform, washing the product with much petrol. ether. Four successive fractions from 3 preparations gave for C and H percentages:

	A.		B.		C.		D.	
I	50.4	3.9	54.9	3.7	54.6	3.9	51.9	3.85
II	50.2	4.8	54.2	4.8	55.2	4.1	50.9	4.8
III	49.5	4.8	54.0	3.8	53.2	4.1	—	—

For the investigations, the fractions B and C with average C=54.52, H=4.08, were used. These agree tolerably well for mono-, di- and trigalloylleucodigallic anhydride, C=55.08—55.18, H=2.9—2.79, except the H is too high.

Acetyl Compounds: When tannin is treated with acetic anhydride, the molecule is split up with formation of penta-acetyldigallic, penta-acetyl-leucodigallic, triacetyl- and diacetyl-gallic acids. On acetylizing in pyridin solution with acetyl chloride, the molecule remains intact, and becomes completely acetylized. The product obtained by solution in acetone and re-precipitation with water to a constant m. p. of 218-224°, analyzed well (combustion, acetyl group Perkin, carboxyl by titration) for completely acetylized tridigalloylleucodigallic acid, the anhydride becoming hydrated by the reaction.

A portion of the acetyl preparation was dissociated by treatment with ethyl chloroformate and KCN; from the amount of carbethoxypenta-acetylleucodigallic acid obtained a ratio of digallic acid to leucodigallic acid of 4:1 in the original tannin is computed.

Acetylization products were obtained by the action of keten upon tannin. It is believed that the hydroxyl groups only reacted, but confirmation is desirable. W. J. K.

Digitized by Google

Constitution of Tannin. R. J. MANNING and M. NIERENSTEIN. *Ber. d. deutsch. chem. Ges.*, 1912 [45], 1546. Glucose has been found in tannin (Kahlbaum, Merck) by Fischer and Freudenberg (ante, p. 502); also Manning (reprint, JOURNAL [5], 573) esterified tannin (Schering) and concluded it to be a glucoside. Nierenstein, however, found that tannin leviss. puriss. Schering yielded no glucose on hydrolysis with alkali (JOURNAL [4], 164). The present authors have therefore esterified the tannin used in Nierenstein's researches (above) and obtained only ethyl gallate, m. p. 156-8°.

It was also found that the rotatory power of tannin decreased gradually on boiling in aqueous solution, hydrogen being meanwhile led through. This has hitherto been explained as a gradual hydrolysis of the complex anhydride into the corresponding acid of weaker optical activity. A definite theory is withheld for the present since in these experiments sugar was not tested for. A 5 per cent. tannin solution (10 cc. = 0.4518 gms.) was used in the research. The non-tans and tans were determined by Körner and Nierenstein's casein method. In addition, the non-tan filtrate was titrated with $KMnO_4$ according to Löwenthal. Trial showed that 10 cc. of 0.1 per cent. solutions of gallic acid, digallic acid and leucodigallic acid required 21.60, 26.70 and 28.10 cc. of 0.05 per cent. $KMnO_4$ respectively. In several cases the non-tans were also examined and found to be optically inactive, which disproves the splitting off of d-leucodigallic acid (also glucose). The $KMnO_4$ values showed further that digallic acid was not present; therefore it was considered that the gain in non-tans was solely gallic acid. The rotation was determined with a 2 dm. tube at 18° in Na light.

	(Non tans (gallic acid)					
H	gms.	cc. found	$KMnO_4$ calculated	Tanstuff gms.	Degrees reading	Rotation + specific
0	0.0244	53.40	52.70	0.4274	5.83	68.22
1	0.0267	56.20	57.70	0.4251	5.65	66.45
2	0.0305	63.20	65.80	0.4213	5.50	65.28
3	0.0316	68.10	68.35	0.4202	5.35	63.68
4	0.0349	74.70	75.40	0.4169	5.30	63.57
5	0.0387	84.70	83.60	0.4131	5.25	63.54
6	0.0425	90.60	91.80	0.4093	5.20	63.53
7	0.0408	88.10	88.20	0.4110	5.00	61.00
8	0.0407	79.70	88.00	0.4111	4.95	60.22
9	0.0489	102.00	107.10	0.4088	4.91	60.04
10	0.0414	84.20	89.50	0.4104	4.92	60.00
11	0.0500	102.40	108.10	0.4018	4.81	59.85
12	0.0532	112.60	115.10	0.3986	4.77	59.84

W. J. K.

Extracts; Highly Concentrated and Dry. WM. AITKEN. *Tanners' Year Book*, 1912, pp. 108-11. Extracts should be dissolved hot. Dry extracts have an advantage over liquid extracts, in that they do not introduce

Digitized by Google

foreign waters having injurious ingredients. (Would not the injurious ingredients be as likely to be present in the dried extract?—Ed.) Instances are cited to show that better results are obtained when liquors are kept warm during tannage.

Tanners' Problems. George Randall. *Tanners' Year Book*, 1912, pp. 63-67. Among the problems mentioned is that of the wisdom of using sodium sulphide or caustic soda in soaking dry hides. No answer is suggested. Another is the proper proportion of acid in handler liquors: no answer. Suggestions are made in regard to methods of drying heavy leathers. Air dried by refrigeration, then moderately heated and forced through the lofts, the writer thinks would be efficient. Methods of buying hides in vogue in England are discussed.

PATENTS.

Evaporator. British Patent No. 6,866. J. MacGregor, Glasgow, Scotland.

Evaporator. U. S. Patents Nos. 1,033,558 and 1,033, 559. Jos. E. Dunn, Philadelphia, Pa.

Evaporator. U. S. Patent No. 1,033,609. P. Muller, Germany.

Evaporator. U. S. Patent No. 1,033,580. W. G. Hall and W. Searby, Hawaii.

Process for the Production of Stock for Leather-board. U. S. Patent No. 1,033,538. A. L. Clapp, Baintree, Mass., assignor to Hide-Ite Leather Co., Boston.

Process for Recovering Nitrogen. British Patent No. 7,394. H. L. Watrigant, Lille, France.

Nitrogen existing in certain waste liquors as albumen, peptone, etc., is recovered by treatment of the liquors with tannin, preferably in the form of tannic extracts, in acid solution. The nitrogenous matter is thereby precipitated alone. If the liquid is then rendered alkaline, the remaining nitrogenous matter is precipitated. The alkaline liquor may receive an addition of aluminum sulphate, ferric chloride, sodium chloride, magnesium chloride, etc.

Hide-Treating Machine. U. S. Patent No. 1,034,783. C. J. Glasel, Cologne, Germany.

Method of Producing Alcohol from Sulphite-Cellulose Lyes. U. S. Patent No. 1,035,086. P. G. Ekstrom, Sweden.

Treating Hides and Skins with Liquids. British Patent No. 9,253. G. B. M. Spigno, Genoa, Italy. This patent relates to driving gear for drums.

Digitized by Google

Tanning-drum.. U. S. Patent No. 1,036,223. CHARLES HAAS, Strassburg. Germany.

Leather-staking Machine. U. S. Patent No. 1,036,335. E. J. F. QUIRIN, Tioga Center, N. Y.

Process of Making Non-slipping Leather. U. S. Patent No. 1,036,267. F. KORNACHER, Auerbach, Germany. The leather is treated with alkali, washed, treated with acid, washed, retanned, and finally treated with a solution of metallic salts.

Evaporating Apparatus. U. S. Patent No. 1,036,637. H. KAYSER, Nuremberg, Germany.

Tanning Compound. U. S. Patent No. 1,036,958. Yellow dock, bugle weed, catechu, hemlock bark and gambier are used together.

Impregnating Leather with Solid Lubricants. English Patent No. 9,320. J. WILLIAMSON, Glasgow. Chrome leather for pump-packings, etc., is impregnated with plumbago, talc or steatite. After tannage and when partly dry the hides are drummed at 140°-160° F. in wax containing the powdered lubricant.

Leather Embossing Machine. English Patent No. 10,232. A. G. BLOXAM, London.

Recovering Chrome Compound from Leather Scrap. English Patent No. 9,462. H. A. VOEDISH and P. KREISMANN, Brantford, Ontario, Canada. The material is kept in a bath of alkaline hydroxide for 2 weeks, washed for a day, placed in an acid bath for 2 or 3 days. The acid and alkaline liquids are then mixed, and the chromium thus precipitated.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII NOVEMBER, 1912 No. 11

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, Hotel Somerset, W. 47th St., New York, N. Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass
C. R. OBERFELL, Harrisonburg, Va.
W. H. TEAS, Marion, Va.
A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

CHANGE OF ADDRESSES.

Alexander T. Hough, to care of Koeboe Houtkop, Maatschapij, Telok Ayre, Pontianak, West Borneo.

David L. Tucker, to Broadway Hotel, Gary, Indiana.

Elting C. Stillwell, to 86 West St., Gloversville, New York.

R. Arnold Seymour-Jones to c/o Messrs. Crosfield & Sons, Bank Quay Works, Warrington, England.

NINTH ANNUAL MEETING.

The Ninth Annual Meeting of the American Leather Chemists Association will be held at Washington, D. C., December 5, 6 and 7, 1912. The committee having in charge the arrangements for the meeting has selected the Hotel Raleigh, Pennsylvania Avenue and Twelfth Street as the place of meeting. A suitable room has been reserved for the meetings, and members who desire to re-

Digitized by Google

tain rooms at the hotel are requested to apply directly to the management. The following is the schedule of prices:

	Per day
Single rooms without bath	$2.00 and up
Single rooms with bath	3.00 and up
Double rooms without bath	3.00 and up
Double rooms with bath	4.00 and up

The following addresses have been arranged for, and will be given at the meeting:—

"How Long Should Chestnut-Oak Bark be Stored before Leaching," C. C. Smoot, III.
"Extract Analysis," C. R. Delaney.
The Identification of Tanned Skins," C. F. Sammet.
"The Geographic Distribution of Tannin Plants," Dr. W. W. Stockberger (of the Bureau of Plant Industry).
"The Disinfection of Hides," F. W. Tilley (of the Bureau of Animal Industry).

Also, the Secretary has arranged for papers from the following, the subjects to be announced later,—

F. M. Loveland, E. J. Haley and Dr. Edmund Stiasny.

INTERNATIONAL ASSOCIATION OF LEATHER TRADES CHEMIST ELEVENTH CONFERENCE, LONDON, 1912.

Report for the JOURNAL *by Douglas J. Law.*

The opening meeting of the Conference took place in the Leathersellers Hall on Monday, September 16, under the Presidency of Dr. J. Gordon Parker. The President welcomed the members in a short speech and other speeches of welcome were delivered by members of the reception committee on behalf of various scientific societies.

Mr. H. Hylton Foster, Master of the Worshipful Company of Leathersellers, extended a welcome from the Court and the Company.

Mr. W. F. Reid, F. I. C., Past President of the Society of Chemical Industry, referred to the backwardness of the British Government in the direction of taking official notice of such conferences and contrasted it with the attitude of other European governments. He referred to the ever increasing scope of industrial chemistry and thought the time might possibly come

Digitized by Google

when industrial chemists would be called upon to manufacture, not only, tanning material, but even leather itself. The electric furnace might, in the future, produce, a material which would be used in the manufacture of leather.

Mr. W. P. Dreaper, F. I. C., welcomed the members as representative of the Institute of Chemistry of the Society of Dyers and Colorists.

Mr. A. Chaston Chapman, F. I. C., President of the Institute of Brewing and representing the President of the Society of Public Analysts, said that he represented an industry which shared with the tanning industry the distinction of great antiquity. Apart from the scientific value of such conferences they were of greater value in bringing one into contact with men hitherto known only by name and friendships might possibly be formed which would last through life.

Mr. F. J. Lloyd, F. I. C., representing Dr. Voelcker, President of the Agricultural Analyst Association, said that the Agricultural Analyst had always, like the leather chemists, to be on guard against fraud. A by-product of the tanning industry—waste leather—was used as an adulterant for fertilizers and there was a great opening for a method by which waste leather could be converted into a substance of real chemical value. The scientific men of the present day were realizing that there was a great gulf fixed between science and supposition. One of the first men to realize this was Pasteur who was the son of a tanner and no doubt in his early days, he realized that what was wanted in every industry was scientific fact and not supposition.

Mr. Sam. Barrow Jun. welcomed the members on behalf of the leather trade and especially the United Tanners' Federation of Great Britain and Ireland.

Replies were then made for the German Section by Prof. Becker; the Italian Section by Dr. Lepetit; the French Section by Dr. Meunier, and the Austrian Section by Dr. Pollak. Dr. Parker also thanked the delegates for their official welcome.

Dr. Parker, in his Presidential address, said that he had no epoch-making discovery to chronicle or new theories to propound, but would content himself with indicating shortly the progress of the Association and express his views as to its future work. The

Digitized by Google

Association started its career in 1897 when it had 19 members, in the fifteen years since then it had grown to its present membership of over 600. In 1898 the late Mr. Franz Kathreiner, whose memory would always be cherished by those who knew him, entered into negotiations with the proprietors of Der Ledermarkt the result of which was that the official journal of the Association was published as a supplement to that Journal. Through the kind assistance of Mr. Dreyfuss the Collegium appeared in 1902 as a four-page supplement which gradually grew to 8 and 16 pages. The Collegium was edited by Mr. Kathreiner until his death when his work was ably continued by Mr. Karl Schorlemmer. After a decision made at the Paris Conference the Executive Committee had now taken over the whole financial and other obligations connected with the Collegium and the journal now consisted of an independently published periodical of 100 pages with an ever growing tendency to expand. With regard to the future his idea was to draw the Association into closer union with the leather and allied trades. He fully recognized the importance of analytical details but more important still was it to obtain results which would be capable of practical application. The problems before the leather chemist were innumerable and almost overwhelming but the darkness in which we groped 25 years ago was gradually being dispersed thanks to the work done by such men as Procter, von Schroeder, Kathreiner, Wood and others. The subject of the preservation and care of raw material was surely worth consideration; the process of salting was convenient and simple but was it either ideal or scientific? He congratulated Mr. Seymour-Jones on the untiring energy which he had displayed in dealing with the subject of authrax and the leather and alied trades owed a debt of gratitude to the Leathersellers Company for their financial support of Dr. Ponder's report on the "Incidence of Authrax." The subject of effluents had become a most burning problem in connection with the establishment of new leather works or the enlargement of existing ones. The leather chemist would find in the lime yard of the tannery, problems of greater financial and scientific interest than disputing over ¼ or ½ per cent. differences in the analyses of tanning extracts. He contented himself with outlining a few questions which require solution; How to

Digitized by Google

produce the greatest yield of pelt from a given weight of raw hides; The merits of the one-pit system of liming against a system with a series of pits; The use of pure lime versus the use of sodium sulphide alone or in a mixture. The questions of plumping and deliming and the deliming action of various acids were becoming of greater importance as knowledge increased and systems changed. The question of bating, puering and drenching had been largely solved by Wood and Becker and their thanks were due to the former for his book recently published, which dealt with the subject in a masterly way. They were within measurable distance of doing away with processes involving the use of animal or bird excrement. Did they thoroughly understand the tanning process? Did they know the correct ratio of tan to acid which should exist in the various stages to produce the best results in the finished leather? Thanks to the recent researches of Procter, Wood and Law the question of plumping and the accurate measurement of the swelling acids was now nearer solution. The leather forming value of the different extracts and materials was an important problem. Was the tanner right in demanding a highly decolorized extract or was this demand creating a product possessing properties of less value as a leather forming agent? He was of opinion that bleaching and decolorizing were seriously deteriorating the tanning extracts and making them of less value as leather-forming materials. Something should be done to check the loss of tanning material which takes place during the tanning process, a tanner who succeeds in combining 75 per cent. of his available tannin with his pelt was certainly above the average. By one means or another 25 per cent. of the leather-forming material originally present in the materials purchased during the year was unaccounted for. Much of this loss was due to ellagic acid or bloom which separated out in the leach house and in the liquors, but there were other causes of loss such as hard water, the cost of perfect extraction, oxidation and fermentation. Mr. Munro Payne had patented a process for dissolving this waste product in dilute alkalies and subsequently recovering it with acid and Nihoul and Paessler had drawn attention to the great losses caused by the use of hard water. Thanks to the researches of Stiasny, Fahrion, Procter, Meunier and others, the chemistry of

Digitized by Google

the chrome and chamois process was better understood than formerly. In the various points he had touched on, there was supplied sufficient to occupy the attention of members of the association for the next 10 or 20 years. The problems could only be solved by patient organized investigation and research and with the co-operation of practical tanners and manufacturers. Referring to the approaching retirement of Professor Procter he was sure he was expressing the wish of everyone connected with the trade when he said that he sincerely trusted that means would be found by which his invaluable services and ripe experience would be retained for the benefit of the trade.

The Seymour-Jones prize of a gold medal and £10 was then awarded to Professor Meunier for his important researches during the previous two years principally in connection with the action of the halogens on skin and gelatin.

Dr. Pollak on behalf of the Austrian Section invited the Association to hold its next Conference in 1914 in Vienna. Dr. Lepetit seconded and Dr. Becker supported the resolution and it was agreed to meet in Vienna.

The meeting then adjourned for luncheon at the Trocadero restaurant where the chair was taken by Mr. Samuel Barrow Jun. in the absence of Sir John Turney.

TUESDAY, SEPTEMBER 17, 9:30 A. M.

The treasurer's report was read and Dr. Auerbach and Dr. Gansser elected as auditors.

The general secretary's report was read; also the corresponding secretaries' reports as follows:

Dr. Paessler, Germany; M. Prevot, France; Dr. Pollak, Austria-Hungary; Dr. Lepetit, Italy; Mr. Van Gijn, Holland; Herr Zeuthen, Scandinavia; Prof. Wauters, Belgium; Dr. Parker, Britain.

Mr. McCandlish, though not present in an official capacity, reported on the state of the American section.

The report of the Editor of the Collegium was then read.

Prof. Meunier was elected President for the next two years and Dr. Paessler as treasurer. Dr. Stiasny was re-elected as Hon. General Secretary.

It was agreed to raise the amount of the subscription to £1

Digitized by Google

per year in order to cover the increased cost of production of the the Collegium.

The following resolution was proposed officially in the name of the German section by Prof. Becker and supported by Drs. Paessler and Philip. "That the Association may, in recognition of distinguished services, elect one or more of their members to the position of Honorary President." The resolution was passed and on the proposal of Prof. Becker, seconded by Prof. Paessler, Prof. Procter was elected to the position of Honorary President.

Technical Agenda.

Professor Procter opened the discussion on the acidity of tan liquors. (Procter and Seymour-Jones, Coll. 464, 5, 6; this Journal, VI, 52-79.) The first question to be decided was, what acids are to be determined and for what purpose is their presence in the liquors desired. Natural tan liquors contained acids of all strengths ranging from acetic and lactic down to gallic acid. The tannin itself had also acid properties. If it was desired to know how much lime the liquor would dissolve there was no better method than the old lime-water titration. To plump the goods a degree of acidity was required comparable to that which turns methyl orange or methyl red.

For the total acid there was no better indicator than hematin. The actual acidity could be determined by the method of the measurement of hydrion concentration by which it was quite easy to titrate to any degree of acidity required. The actual part played by the acid in the tanning process was not yet worked out, it was well known that neutral tannin and gelatin do not precipitate. He recommended that 2 or 3 indicators such as methyl orange, methyl red and congo red should be used for determining the degree of acidity as regards its plumping effect, lime water should be used for determining lime-dissolving power and hematin for determining the total acidity. These estimations should be carried out and the progress of the tanning action observed at the same time.

Mr. R. A. Seymour-Jones agreed that the function of the acids in the tanning process required investigation before much time was spent in devising methods for their estimation. There were three entities concerned in the tanning process, hide acid and

Digitized by Google

tannin. The system hide-acid had been investigated very thoroughly by Professor Procter. What required investigation was the effect of an acid-modified tannin on the acid modified hide?

Mr. H. G. Bennet said that the acidity of the tannin itself did not require to be estimated and this fact condemned most of the existing methods. With strong liquors the tannin should be previously removed or preferably they should all be made to a constant strength of tannin before titration.

Prof. Procter replied that the tannins are themselves acid and their acidity should therefore be estimated. Some of the tannins had sufficient acidity to swell hide.

Mr. J. T. Wood spoke of the effect of neutral salts in the tan liquors which had been investigated by himself and Sand and Law.

Dr. Turnbull emphasized the importance of the history of the tan-liquor in the investigation of its acidity. He had found that, with liquors from the same tan-yard the differences between titrations with lime-water and using methyl-orange as indicator were very constant.

Dr. Gansser opened the discussion on the use of animalized cotton in the examination of tanning extracts. (Gansser, Collegium, 509, 479-482.) The control of the color of extracts was most important and the method of measuring the color of the solution itself was unsatisfactory as were also tests made using skin as testing medium. The tintometer method of testing the color of solutions of extracts immediately after dissolving was unsatisfactory as their color changed greatly during the tanning process. Of various textiles tried, cotton fiber was the most satisfactory and served simply as a skeleton for holding the gelatin which was fixed with formaldehyde. The cotton was sufficiently protected by the gelatin to prevent abnormal results occurring through its affinity for any aniline dye which might have been used for artificially coloring the extract under examination. From experiments made it seemed as if valuable information with regard to weight-giving properties and strength could be obtained by the method. Animalized cotton treated with quinone showed a great increase in strength which amounted in some cases to 40 per cent. This increase of strength was also seen when the quinone treatment was combined with a tanning

Digitized by Google

process. Quinone had thus the same strengthening effect as it had on vegetable or mineral-tanned leather. The color given by an extract in the animalized cotton was not identical with that given on skin, but that the differences were constant.

Dr. Lepetit said that he had made experiments following Vignon's proposal to use silk, but was not satisfied that Gansser's material was the most standard.

Dr. Turnbull referred to the fact that hide was stronger before tanning than it was after whereas, with animalized cotton, the reverse was the case. The precipitate apparently cohered the fibers.

Dr. Auerbach said that the tanner wanted to know the color given on skin by an extract and not that on animalized cotton and referred to the possibility of standardizing pelt.

Dr. Paessler had tested the method and found the color different to that obtained on leather.

Prof. Schneider advocated the use of pelt moderated with alum or titranium which made a sensitive medium for showing differences of color given by extracts.

Dr. Gansser said that he suggested the method as an auxiliary one and as a standard. Fading and darkening could be conveniently tested by the method. If an accurate estimate of color was required the test must be done under the same conditions and on the same skin.

Prof. Paessler then described his experiments with Kallab's apparatus on the behavior of leather against light. (Collegium 1912, 287-289).

With the apparatus, 6 hours exposure on tanned or dyed leather had the same effect as 28-36 hours in ordinary daylight. He mentioned a case in which shoes of glazed kid, dyed brown turned greenish on exposure to light. By the means of the apparatus he was able to show that the effect was due to the action of light on the dye and chrome in the leather. A number of photographs were shown on leather which had simply been exposed to light under the negative. A curious part was noticed with leather tanned with *Cassia auriculata;* for 28 days the leather was gradually darkened by exposure to light but after a longer exposure the darkened portions commenced to become

Digitized by Google

bleached till their tint was appreciably lighter than that of the original leather.

WEDNESDAY, SEPTEMBER 18. 9:30 A. M.

Mr. Wood opened the discussion in the report of the referees on the control of lime liquors and wet work. (Wood and Law. Collegium, 1912, 121-129; this Journal, July, pp. 346-58.) The following scheme of analysis of lime liquors was submitted for discussion:—

(1) For analysis the liquors should be filtered through S. & S. 605 filter paper.

(2) *Alkalinity* by titration of the filtered liquor with decinormal acid, using methyl-red as indicator. This gives the total alkalinity.

(3) *Ammonia* by acidifying 100 cc. of the unfiltered liquor with HCl until acid to methyl-orange, adding excess of magnesia and distilling into standard acid.

(4) *Sulphides* by titration of the filtered liquor with decinormal zinc sulphate in the presence of ammonium chloride, using sodium nitro-prusside as external indicator (Blockley & Mehd, J. S. C. I., 1912, 369-372; this Journal, July, pp. 358-68).

(5) *Nitrogen* by Kjeldahl's method on 25-50 cc. of the filtered liquor. Degree of hydrolysis by a combination of the figures obtained by the Kjeldahl method and Stiasny's formaldehyde titration (Collegium, 1910, 181-187; abstr. this J., 1911, pp. 345-6).

Professor Procter proposed a vote of thanks to the referees and recommended that the proposed methods should be adopted.

Dr. Lepetit proposed and Prof. Meunier seconded that the methods proposed should be adopted as the official method.

Mr. Bennet proposed that the methods should only be recommended and that comparative tests should be carried out by different observers.

Dr. Stiasny referred to the difficulty of filtration and said that different methods of filtration should be used for different estimations. All calcium carbonate should be eliminated before titration for alkalinity and it was preferable to centrifuge the liquor only before estimating the nitrogen. As an indicator phenolphthalein had no sharp end-point while methyl-red showed some of the products of hydrolysis of hide-substance. The hydrolytic decomposition products were of two classes, one of which was

Digitized by Google

precipitated by acids and could be estimated by Kjeldahl's method after thus precipitating and the other which was estimated by the formaldehyde titration.

Dr. Parker said the difficulty of the tanner and chemist was to say, how much of the nitrogen in solution in the limes would have made leather and remarked that sulphides dissolved other substances from the skin than did lime.

It was decided that the scheme of analysis outlined should be the provisional method until the next conference.

Prof. Paessler described briefly his experiments on the denaturization of salt. (Collegium, 1912, 379-388).

Prof. Becker introduced the subject of salt stains and described his experiments in conjunction with Prof. Paessler on the subject (Collegium, 1912, 408-418). Prof. Kohnstein had stated that salt stains could be avoided by the use of petroleum for denaturizing the salt. Abt had found sulphates and phosphates in the region of salt stains in leather. From the fact that various kinds of salt stains bite into the skin he had come to the conclusion that they were of bacterial origin. There were always crystals of salt lying immediately over the stain in the salted hide. He had succeeded in isolating the bacteria from the various kinds of stains and had been able to produce similar stains from a pure culture of the same bacteria. These artificial salt stains had been produced both on gelatin and on skin and were more easily produced on raw skin than on limed skin. The influence of salt was favorable to the bacteria and successive increases in the salt in the gelatin from 1-10 per cent. produced successive increases in growth of the bacteria. Alkalies are also favorable to the growth of the bacteria and the most rapid growth is at 25 degrees C., the higher the temperature up to a certain point, the deeper being the stains. The phosphates and sulphates found by Abt were due to bacterial action. To avoid salt stains some sterilizing process is necessary. Freezing is probably effective but infection may take place subsequently, the use of tar is not recommended. Organic acids would be effective but the use of formic acid would entail a swelling of the hide and consequently more water in it. Mustard oil is one of the best sterilizing agents and the suggestion of Schmidt to use zinc chloride was practical. Salt is a perfect preserving agent if properly used and the addi-

Digitized by Google

tion of 3 per cent. of Sodium carbonate will prevent bacterial growth. The use of finely powdered salt was preferable to large crystals. Most stains occurred where slaughter-houses were dirty and the salt was used more than once and put on the hides before they had become cooled. If soda is used with the salt as a sterilizing agent it must be thoroughly removed from the skin before tanning or a loose spongy leather is produced.

Dr. Abt describing his experiments on the origin of salt-stains (Collegium, 1912, 388-408, this Journal, VII, 492-7) said that the sulphates which he had found in the stained portions were derived from calcium sulphate which was sometimes present in salt to the extent of one-half per cent. The phosphates were derived from the nucleic acid of the cell. The first origin of the stains was due to small grains of calcium sulphate in the salt. The stains he had investigated were different from those described by Dr. Becker. The stains are turned black by ammonium sulphide through the formation of iron sulphide and nearly the whole of the original color of the stains can be removed by washing with dilute acid. The action of tan liquor turns the yellow stains brown or black and this effect would not be produced if the color were due to bacteria. No loss of skin substance could be found by comparing stained and unstained portions of the same skin and no bacteria could be found inside the skin by staining methods. In another kind of stain no calcium phosphate could be found in the leather, this stain was seen in skins from sulphide limes and was nearly black but was entirely removed by acids. It was seen frequently on horse hides which had been badly flayed and was due to iron bicarbonate formed from carbonic acid derived from fermentation. If phosphates are found in the stains is may be concluded that they are due to calcium sulphate in the salt which must therefore be free from that substance. If no phosphates are present the stains are bacterial and must be avoided by using antiseptics. The use of soda in salt is advisable to avoid salt stains, the calcium would then be precipitated as carbonate and the soda would also act as an antiseptic and dehydrating agent.

Professor Procter said there were two classes of stains, one class of which was certainly due to iron. The latter were green in sulphide limes and yellow in white limes, they became blue on

Digitized by Google

entering the tan-liquor and disappeared during the tanning. With these stains there was no bacterial action or destruction of the grain. He had seen bluish stains in plaster kips which had made liming and unhairing difficult. The earth with which they were coated consisted principally of sodium sulphate with a little sodium carbonate and ferrous carbonate. When these hides were stored in a damp warehouse the iron acted on the hides, the action being due to the effect of water and carbon dioxide in forming iron bicarbonate. The difficulty of swelling when organic acid were used as disinfectants could be avoided by using salt when a dehydrating effect would be produced.

Dr. Andreis said he had avoided salt stains by throwing the hides over a horse to drip after salting when the blood etc., ran away. If this were done many stains would not occur.

Dr. Baldracco mentioned that the use of sodium fluoride to the extent of one per cent. on the salt would avoid salt stains.

Mr. Charles Parker said harm had previously sometimes been done by chemists putting ill-digested information before the tanners. They would prefer to wait till the chemists had thoroughly tested the subject in a scientific way before taking it up.

Mr. J. T. Wood said that salt-stains were not necessarily due to the denaturizing medium in the salt as they were very prevalent in England, where the salt was not denaturized. The point raised by Dr. Abt regarding the penetration of the skin by the stain might be explained by the products of the bacteria penetrating and not the bacteria themselves.

Mr. A. Seymour-Jones said the primary step to be taken was to keep the slaughter-houses clean and the question of the purity of the salt and the antiseptic added to it were the main ones.

Dr. Becker said he was unable artificially to produce stains by using gypsum or phosphate. He suggested that tanners should test the mixture of salt and sodium carbonate.

Thursday, September 19.

The following were elected to form the committee for the investigation of salt stains under the presidency of Mr. Seymour-Jones, Dr. Abt, Prof. Baldracco, Prof. Becker, Mr. Charles Parker and Mr. J. T. Wood.

Dr. Parker then referred to the soaking of skins by means of

Digitized by Google

organic acids. From his experiments the increase of pelt weight when formic acid was used was 1-3 per cent. and in dry hides 5 per cent. compared with other methods. The hides were soaked in water over night and then suspended in a ⅕-¼ per cent. formic acid solution for 12-18 hours, handling once or twice. They were then drummed for an hour or two and placed in water overnight. They then entered the limes and any rubbery condition produced by the acid disappeared after 4-6 hours. The cost of the processes is low, being less than ½*d* her hide. Alkaline substances must be removed before entering the formic acid.

Prof. Procter suggested the use of sulphurous acid as it was cheap, bactericidal and easy to handle.

Dr. Abt reported the experiences of several French tanners with the formic acid and said they had found that the grain was not so fine as desirable after the process. They believed that alkaline swelling produced a finer grain than acid swelling.

Prof. Procter said it was possible that acids and alkalies act differently on the grain because there are different parts of the collagen molecule which react with both reagents. The pickling-process which was an acid swelling, produced a nice grain so he should think that the method of applying the formic acid was responsible for the defect. The excess of acid must be removed before placing the hides in lime.

Mr. Alfred Seymour-Jones suggested that hides should be restored to the wet condition and sterilized at the port of shipment so that they arrive at European tanneries in a thoroughly sound condition.

Dr. Parker said that formic acid gave a better yield of weight than lactic acid or any other organic acid. He agreed with Dr. Abt that rather a rough grain was produced if the acid were used too strong, but any roughness disappeared in the liming process.

The question of sulphite-cellulose liquors and their value in leather manufacture was then discussed. Dr. Parker said there were many different materials which give a product something like leather and sulphite cellulose was one of them. The product obtained depended entirely on the treatment of the extract and the conditions of working. What should be avoided was the adulteration of ordinary vegetable extracts with the material.

Digitized by Google

which mixtures, in his experience, gave worse results than the sulphite cellulose itself.

Mr. Thuau reported some successful experiments he had made with wood-pulp. The hides were just half tanned with extract, then treated with wood pulp and finally given another vegetable tannage.

Prof. Procter agreed with the possibility of using material in the manner referred to. The aniline test was sensitive enough to detect any addition of wood-pulp to extracts but sulphited extracts treated under pressure gave a slight positive test.

Dr. Lepetit suggested the comparison of the gravimetric and Löwenthal's analysis to detect the presence of wood-pulp and suggested that every record of tannin analysis should contain the statement whether the extract was free from wood pulp or not.

Prof. Schneider suggested gradual extraction to remove the lignin from the resinous matters.

Professor Paessler said he had calculated the real price of the tanning matter in the wood-pulp and found it to be 80-90 pf. per kilo., hence it was not even commercially advantageous to use.

Dr. Auerbach did not believe in the tanning capacity of wood-pulp because, even in mixtures, the wood-pulp could be washed out of the leather. He agreed with the possibility of using it as weighting material in place of sugar and molasses. There were wood-pulp extracts on the market containing 15 per cent. of lime.

Mr. Thuau then read the report of the Commission for the investigation of the analysis of leather published in Collegium, 1912, 500-517 (pp. 602-7, this issue of the JOURNAL).

On resuming after lunch Dr. Parker informed the meeting that the Executive Council had suggested that the Association should contribute the sum of £100 to the fund for the scheme of a Procter Research Laboratory which had been started.

The following were then elected to the Commission for the analysis of oils and fats under the chairmanship of Dr. Fahrion, Mr. Thuau, Mr. Bennett, Mr. Brumwell, Mr. Wood, Dr. Baldracco, Mr. Van Gijn and Dr. Paessler.

Digitized by Google

Dr. Stiasny then opened the discussion on the question of the qualitative detection of vegetable tannins referring the members to the papers published in Collegium, 1911, 318-332; 1912, 483-499 (Journal, VI, 479-96, and VII, 548-69).

Dr. Paessler described a method he had evolved for the detection of mangrove in quebracho which consisted in weighing the precipitate produced by ammonium molybdate with the solution. The molybdate figure for quebracho extract was 27-36 while mangrove gave 120-140. He suggested that the method should be tested.

Dr. Auerbach said he had found wood-pulp extracts which did not respond to the lead acetate-sodium hydrate test owing to the treatment which they had received. He was unable to obtain satisfactory results with the methods of Schell & Kohnstein.

Dr. Pollak proposed a method of treating extract solution with chlorine and extracting the precipitate with ethyl ether and acetic ether, the proportions of the two extractions being 1-1 in the case of quebracho and 4-1 in the case of mangrove.

Prof. Meunier reported on Tannery Effluents, he considered the question easy of solution. It was advantageous that all the liquors should mix when the solid matter will be effectually precipitated. Especially should the vegetable and mineral matters mix in the settling tanks. Chlorine as it is present in wood-pulp in the effluents from paper-mills precipitates many of the matters in tannery effluents and it is very advantageous if the two effluents can be mixed. Air and light are important factors. The sediment was rich in nitrogen but the prohibitive cost of drying would prevent any use being made of it.

Prof. Meunier then described his work on the action of alkali carbonates in the formaldehyde tannage (Collegium, 1912, 54-56; 420-423). He found that pelt which had been treated for two hours in a saturated potassium carbonate solution soon dries out to leather which has the sole disadvantage of being non-resistant to water. Solutions of less strength had a dehydrating action and the role of the potassium carbonate in the formaldehyde tannage is an important one as formaldehyde alone does not give a satisfactory result while a previous dehydration with potassium carbonate or hyposulphite materially improves the result.

Digitized by Google

Prof. Procter said that many years ago he and Mr. Seymour-Jones had tried to replace potassium carbonate with salt and sodium hyposulphite in the formaldehyde tannage.

Mr. Seymour-Jones said that the use of sodium hyposulphite had an accelerating effect on many tannages.

Prof. Procter, in introducing the subject of tannin analysis said that the official method worked well and gave as concordant results as could be expected. He proposed that in those cases in which the filter-bell method was demanded that it should be applied according to the rules of the German Section using Paesslers lightly-chrome hide powder. The proposal was accepted. It was further agreed that the Commission for tannin analysis should not be reappointed and that the matter should be allowed to rest.

Dr. Gansser proposed that in cases where the analysis of pure sulphite cellulose is reported that it should not be described as tanning matter but either as "matter absorbed by hide" or "pseudo-tannin." After a short discussion in which Dr. Auerbach, Dr. Gansser, Dr. Stiasny and Dr. Turnbull took part, the proposal was accepted by a majority of 24-17.

Prof. Procter then reported on the colorimetric method and urged the members to use the new method provisionally as agreed upon at the last conference.

Dr. Stiasny thanked the Leathersellers Company for all the kindness they had shown and proposed that a letter expressing their thanks should be sent, which was agreed to.

Prof. Meunier then expressed thanks for the excellent way in which the conference had been conducted by Dr. Parker, who suitably replied and the conference then closed.

On Friday, September 20, the members and guests to the number of 80 travelled to Windsor, arriving there at 10:30. The State Apartments and St. George's Chapel of Windsor Castle were inspected during the morning and lunch was taken at the White Hart Hotel. In the afternoon an excursion was made by special steam-launch to Maidenhead, tea being served on board.

Digitized by Google

REPORT OF THE INTERNATIONAL COMMISSION ON LEATHER ANALYSIS.

Condensed translation from *Collegium*, 1912, 500-17.

By Urbain J. Thuau.

At the last Congress of the Association in Paris in 1910, many opinions were expressed in regard to the methods employed in the analysis of leather. Prof. Meunier demanded that an effort be made to arrive at clear conclusions, since several governments would wish to employ such methods as would be agreed upon in the specifications for leather for military purposes. Analysis alone would not be sufficient to fix the quality of the leather, but it should be accompanied by various physical tests; impermeability, resistance, etc. For a sample he proposed a strip perpendicular to the line of the back at the shoulder. He objected to powdering the sample, difficult in the case of leathers with much grease and liable to injure the composition of the leather in consequence of heat developed. Professor Paessler preferred a disintegrating mill. Professor Appelius thought the part between neck and butt (croupon) suggested by Meunier afforded the best average sample. Mons. Godfrind insisted upon taking three samples from different parts, and upon the cutting up of the sample by means of special shears. Mons. Dacosta said that it was necessary to fix the exact size of the pieces in order to obtain concordant results. Dr. Turnbull noted that the samples taken would be different, depending on their purpose, which is sometimes simply comparative, and sometimes for an absolute analysis. He favored reducing the sample to powder. Prof. Kohnstein said that it is impossible to regulate absolutely the taking of samples, or the fineness of the prepared sample. Mons. Thuau expressed a preference for the taking of uniform samples, and for the employment of the microtome.

After further discussion the Congress adopted two resolutions proposed by Prof. Procter, (1) that the sample should be taken in such a fashion as to represent the average composition of the leather; (2) the sample shall be comminuted with a cutting instrument, preferably a microtome. The Congress agreed unanimously to the appointment of a commission to consider the subject, composed of the following gentlemen:

Digitized by Google

Germany, Messrs. Appelius, Jablonski and Paessler.
Belgium, Messrs. Godfrind and Sody.
England, Messrs. Turnbull and Arnold Seymour-Jones.
Austria, Prof. Kohnstein.
United States, Mr. W. K. Alsop.
Italy, Mr. Baldracco.
Denmark, Mr. Boegh.
France, Messrs. Meunier, Thuau, Dacosta and Jouve.

The commission elected Prof. Kohnstein as President, but they were not able to hold enough meetings to go over together the various problems and agree upon a line of work to be followed. A sample was prepared by Messrs. Thuau and Dacosta and sent out to each member of the commission with a circular describing the work to be done. The sample was taken from a butt ("croupon") at right angles to the line of the back, next to the neck. The piece was cut into strips which were put through a microtome and cut into shavings 1 mm. thick. 1,500 gr. of these fragments were placed in a glass vessel and rotated for 4 hours. The whole was then distributed into 30 clean dry bottles, corked and sealed and labelled D. T. (Dacosta Thuau). To each member of the commission were sent two of these bottles and the following circular:—

I. *Water.*—Employ the ordinary method of the laboratory. State how many hours were required to obtain constant weight. Describe drying apparatus.

II. *Ash.*—Use the ordinary method of the laboratory; describe it.

III. *Ash* (2).—Use an alcohol burner instead of gas, comparing the ash with the preceding. Illuminating gas may produce SO_3 which combines with bases to increase the quantity of ash.

IV. *Water Extract.*—Ordinary method. Use Koch's apparatus (112 hours under pressure of 1 meter of water, then extracting 1 liter in 2 hours at the temperature of the laboratory). State the volume of the Koch's apparatus employed, the temperature of the laboratory, and the residue from the distilled water employed. Determination of tannin and non-tannin in water extract optional.

Digitized by Google

V. *Water Extract* (2).—Put 5 g. of leather in 250 cc. water in a bottle of 500 cc. capacity, and put on rotary shaker, 40 revolutions per minute, for 5 hours. Filter, and in the filtrate determine tannin and non-tans by either shake or filter-bell method. This new method for water-extract is very practical and more precise than that with Koch's apparatus. State with the results the residue from the distilled water, the volume of the shaker bottle used, filter paper (Schleicher if possible), etc.

VI. *Fatty Matter.*—With a Soxhlet. Use petroleum ether boiling below 70° C. or chloroform. Give details of the process and state solvent employed.

VII. *Nitrogen by Kjeldahl Method.*—Describe steps. Do this in duplicate.

VIII. *Nitrogen by the Method of Thuau and de Korsak.*—For this optional method see *Collegium*, 1910, No. 425, p. 364. (Abstr. this JOURNAL, V, 527.)

IX. SO_3.—Ballan and Maljean's method. Ash over an alcohol burner, and determine SO_3 by $BaCl_2$. Again ash over alcohol burner after adding Na_2CO_3, and then estimate total sulphates. By difference find free SO_3. For details see *Collegium*, 1906, No. 189, p. 15. In this description replace gas burner by alcohol burner.

X. SO_3 *by Kohnstein's Method.*—See *Collegium*, 1911, No. 475, p. 314. (Abstr. this JOURNAL, VI, 603.)

XI. SO_3 *by Meunier's Method* (with Mahler's bomb). See *Collegium*, 1906, No. 221, p. 259, 4th method.

XII. SO_3 *by the Method of Paessler and Arnoldi.*—See *Collegium*, 1908, No. 326, p. 358.

XIII. *Glucose* in the water-extract or otherwise, either by the gravimetric method or by the volumetric method of Fehling, or by the polarimeter. Explain the method employed and give details.

XIV. *Mineral Matters in the Ash*, if it seems worth while.

XV. *Experiments in Estimating Total Acidity* of the leather, (organic and free mineral acids). Explain your ideas on this subject and give details.

Digitized by Google

XVI. *Any other Experiments.*—Please communicate at once to the members of the commission the methods tried, in order that results may be compared.

Only Messrs. Meunier, Paessler, Appelius, Kohnstein, Baldracco, and Thuau did in part the determinations proposed, on the sample D. T., and sent in their results, summarized in the table.

	Moisture	Ash (gas)	Ash (alcohol)	Water extract Koch's app. ordinary temp.	Water extract agitator ordinary temp.	Extract by petroleum ether
Appelius	19.2	0.80	—	5.09	6.08	0.56
Baldracco	19.7	0.70	0.72	3.77	—	0.41
Kohnstein	20.2	0.65	—	6.28[1]	4.92	0.45
Meunier	19.2	0.80	0.59	4.52	5.30	—
Paessler	19.1	0.60	—	4.60	5.30	0.70
Thuau	19.5	0.60	0.44	5.00	6.10	0.50

	Nitrogen Kjeldahl	Combined SO_3 Balland & Maljean alcohol	Total SO_3 Balland & Maljean alcohol	Free SO_3 (deducting 0.14 for S. in the hide)	Glucose in the water extract	Invert sugar in water extract
Appelius	7.76	0.08	0.27	0.05	0.21	0.02
Baldracco	6.92	0.10	0.34	0.10	—	—
Kohnstein	8.01	--	--	--	0.67	—
Meunier	7.19	0.04	0.57	0.39	—	—
Paessler	7.81	--	—	—	0.30	0.00
Thuau	7.34	0.05	0.29	0.10	0.35	—

[1] With percolator at 40° C.

Besides these results, Paessler found 0.6 per cent. ash by the electric furnace, 0.097 per cent. SO_3 by his method, and 7.5 per cent. nitrogen by Thuau and deKorsak's method. Kohnstein found 0.04 per cent. SO_3 by his method.

The reports of the several members of the commission are given in full. We select from these reports a few points of interest, chiefly matters in which the methods used differ notably from those of the American Association.

Nitrogen.—Appelius used 0.6 g. leather, 10 cc. H_2SO_4 and 0.7 g. mercury. After digestion he added 2 g. K_2S in 40 cc. H_2O, a little powdered Zn and 60 cc. of a 5 per cent. NaOH solution. The NH_3 was received into 50 cc. N/10 H_2SO_4 and titrated back with N/10 soda, "tournesol" indicator. Baldracco used mercury in the digestion. Kohnstein used Wilmarth's modification of Kjeldahl's method, receiving the NH_3 into N/5 HCl.

Digitized by Google

Meunier digested 0.65 g. of leather with 25 cc. H_2SO_4, 10 g. K_2SO_4 and 5 g. anhydrous $CuSO_4$. Paessler's method was almost identical with that of Appelius.

Sulphuric Acid.—Appelius tried Kohnstein's method, with unsatisfactory results. Paessler remarks that the sample contained a little aluminum, and if this were combined with SO_3, it would be necessary to deduct from the figure for free SO_3, the amount combined with Al.

Glucose.—Appelius and Paessler used von Schroeder's method, differing but slightly from that of the A. L. C. A. Meunier strongly recommends Bertrand's method: (*Bull. Soc. Chem.*, 1906; vol. 3, p. 1,285.)

Mr. Arnold Seymour-Jones reported his work on several samples of leather, other than those sent out by Thuau and Dacosta, the work having been done before those samples were received. He found that extraction with CS_2 and with petroleum ether gave practically identical results for fat. Ash was determined by a Teclu burner, a muffle, and an alcohol burner. No increase in weight of ash was observed in the case of the gas burner. The Rouchèse method for N is condemned. In the Kjeldahl method an error may be introduced by the use of an active oxidizing agent in the digestion. In such cases a part of the N is liable to escape as HCN. Digestion with concentrated sulphuric acid alone is recommended, with the smallest possible flame. In distilling over the NH_3, a small excess only of NaOH should be used. Further researches are necessary to determine accurately the N content of the various kinds of skins used by the tanner.

For determining glucose, Mr. Jones used the volumetric method of Fehling, the gravimetric method of von Schroeder and the method of Wood & Berry (*Collegium*, 1909). The first of these is recommended because of its rapidity and accuracy. Mr. Jones also prefers Wood & Berry's method to that of von Schroeder. He tried a number of experiments in the determination of free sulphuric acid, but without success. He finds the method of Procter and Searle satisfactory in most instances. That of Wünsch gives good results, but is too elaborate. That of Ballan and Maljean is not superior to the Procter-Searle, and is hardly so convenient. Kohnstein's method is open to serious theoretical objections.

Digitized by Google

In conclusion, the compiler of the report remarks that the results are not so concordant and conclusive as to furnish a basis for recommendations as to an official method.

ARE YOU KEEPING PACE WITH CHEMISTRY?[1]

By Prof. Henry R. Procter.

Our editor has again asked me to contribute something to his semi-annual number, and as I am anxious to meet his wishes, but have nothing particular to say, I do not think I can do better than take as my text a post-card to hand this morning, which though posted in "London, England," seems to me stamped with the genius of the States. It begins "Are you keeping pace with chemistry? Or are you getting along on what you knew when you graduated? Are you posted on the radio-active elements, rare gases of the air, colloids, decomposition of molecules and atoms, electrolytic processes, ionic equilibrium and chemical affinity? or on enzyme action, synthesis of physiological compounds, and the stereochemistry of the sugars? We furnish the books that will make you a chemist of to-day."

I pause here, since our Editor objects to gratuitous advertisement; but you will doubtless consult the proper columns, for surely everyone of us will be anxious to put down his five dollars for such an end! If it could but be done! I have been studying chemistry for 50 years, and am still only in the undergraduate stage, though I have an honorary degree. One keeps on learning, but those tiresome investigators are always ahead, and one can never really catch up. Nevertheless the menu which is offered is an attractive one.

Radio-activity and rare gases have not yet done much for tanning, but the rest are mixing themselves up with leather manufacture in a quite bewildering way. Almost everything concerned in the production of leather is colloidal, but the best experts are not yet clear as to the nature of the colloid state. What makes the colloid particle behave so like a molecule, and what is the cause and nature of the electric charge which gives

[1] *Shoe and Leather Reporter*, Sept. 19, 1912.

Digitized by Google

it its affinities, and how far is it subject to the "mass-law" which governs ionic equilibrium?

It looks as if almost any colloid salt could tan. The more basic, and consequently the more colloid we make our chrome salt, the more heavily it tans; and apparently something of the same sort is true of the vegetable tans, of which the weight-giving elements seem all in a complicated and very colloid condition, like the "reds" of hemlock so difficult to filter; while simple tannins such as gallotannic acid all give light leathers.

Perhaps if we knew how to regulate their colloidal division we might get all the weight we want, without troubling about the "stereochemistry of sugars." Certainly if we could introduce the tans into the leather as true crystalloid solutions and convert them on the fiber to the colloid form, as in the two-bath chrome process, we could reduce our tannage to hours and probably still get weight.

Then the old question of acidity of liquors crops up, at which you have worked so much on your side. Your chemists have devised half a dozen processes for estimating it, and we have added two or three more, all giving different results, because we don't clearly know yet what we want to estimate; and still less do we know what it does in the yard, or even what is the quantity we ought to aim at for the best results. And yet one is certain that acid, and the exact quantity of it, must play a most important part in the manufacture of leather. Without acid (or some other electrolyte which plays its part) many colloid solutions cannot exist, which are yet equally destroyed by a trifling excess.

There is, or used to be, a medicinal iron solution, "Fer Bravais," which was made by placing ferric chloride in a parchment paper cell surrounded with pure water which was constantly changed. The hydrochloric acid passed out into the water, leaving in the cell a dark brown colloid solution of practically pure ferric oxide. If you removed the last minute traces of acid, it precipitated. If you diluted it with water it precipitated, if you added acid or alkali or salts it precipitated. Pretty much the same thing can be done with chrome, and in fact happens in chrome tannage. Colloids are like that; marvelously unstable

Digitized by Google

under certain conditions; and we cannot wonder that leather manufacture still presents problems.

Another article on our list is "enzyme action;" the effect of those strange organic compounds, as yet only produced by living cells, which bring about (or perhaps more strictly hasten) chemical changes of the most varied description without suffering change themselves. The growing cell of the barley in malting produces such a substance, diastase, which is capable of converting at least many thousand times its weight of starch into sugar in a few hours, which the change if unaided would take years or centuries. Other enzymes convert fats into emulsions, set free fatty acids, dissolve the epidermis structure of skin, or its fiber, or interfibrillary cementing substance; each enzyme doing its own particular work, without touching the things outside its range. The puering process is mainly due to the action of such enzymes, in that case largely produced by bacteria, but in "Oropon" these are substituted by the enzyme of the animal pancreas, and by purely chemical salts. Oropon is, for many classes of leather, a thoroughly satisfactory substitute for the disgusting and dangerous puer; but it is not the "last word" in enzyme bates, nor pancreatin the only enzyme. I was in a chrome works the other day, which turns out most successful chrome calf, where no puer has ever been used, but merely chemical deliming aided by special enzymes.

But I must not enlarge further—time and other work, if not the Editor, forbid it. And indeed, this is much in the nature of a sermon, convincing to the converted, but hardly likely to affect the heathen and the unregenerate. It will have served its purpose if it fills the allotted time, and fans a little the sacred flame where this is already alight.

THE PROCESS OF LIMING.*

Lecture by Cav. Uff. Ettore Andreis.

Whoever, as a practical man, has occasion to visit a tannery will note, even in the best conducted works, that the process of liming is usually carried out in a perfunctory manner, al-

* *Leather Trades Review*, XLV, 506-8, 593-5.

Digitized by Google

though, in reality, it is one of the most important operations in the tannery. Liming is still considered by many tanners as a method used solely for removing the hair from hides, quite overlooking the fact that there are matters of far greater importance to study during the process. No wonder, therefore, that the finished leather is frequently below expectations as regards quality in cases where the process of liming is so obviously neglected, and that steps are subsequently taken to trace the cause of the poor results. These primary errors are often the source of trouble with pelts which is reflected on the quality of the finished leather.

The process of soaking is nearly always the same that has been practiced from time immemorial; therefore, many tanners argue that that process cannot be the cause of the damage. In the first place the salt is completely removed. The hides were well soaked, and brought back to their original condition. At the proper time the exact quantity of fresh lime was given in the usual proportions. The process was continued during the prescribed time; in short, nothing out of the ordinary routine was done, yet some hides have not released their short hairs (although this depends to a great extent on the nature of the skins). The final operations are then carried through as usual, without any apparent difficulty. But raw hides must be treated according to their natural characteristics, otherwise so many things may occur which would give cause for complaint.

Finally, some considerations are given to the treatment of the hides in the pits or vats, to find the cause of the failure to produce first-class leather and the extent of the inferiority. It is sometimes found that the finished product is too hard or too soft, even spongy. The causes are sought without finding the source of the trouble and without arriving at any satisfactory result. As the witty carabinier of the fable said, "When the dead man was questioned, there was no suitable reply."

There are many tanners who still consider the tannage proper as the only important process, and that the quality of the resultant leather depends on it. On the other hand, some tanners prefer to examine more closely the preliminary operations of soaking and liming, which they believe to be the most important and complicated processes in the production of leather. These processes I would call the keys to success in leather

Digitized by Google

manufacturing. It is certainly impossible, nor is it within the scope of this lecture, to give a clearly defined account of the process of liming, nor is it my intention to submit the physical operations of the process to a special examination, but, if possible, I intend to set forth clearly some of the important duties that should be fulfilled in a rationally conducted method of liming, where the hides treated are more particularly desired to be converted into soft, pliant leather, whether for saddlery, bags, bookbinding, or belting purposes, as produced from sheep, goat, and calf skins and cow hides by the ordinary vegetable processes of tanning.

The principal and absolutely necessary properties of this class of leathers are (1) strength, (2) pliability, and (3) mellowness, but, above all, strength is required. If these qualities are completely combined in the finished product, the leather is likely to satisfy all requirements. These qualities, I will say at once, cannot possibly be obtained in their highest perfection if the loosening of the fibers of the skin has not been carried to an exact point during the process of liming; just so far as this degree of relaxation is not reached, so will the leather be correspondingly defective.

As has been noted, skins in their natural state, as taken from the animal, are never in a suitable condition for tanning, however soft and pliant they may be. The cellular tissues of green hides are closely and firmly interwoven, almost, as it were, contracted, and are filled with the true skin substance, likewise with foreign matters, such as blood, humors, impurities, etc., which must be completely eliminated for the purposes of leather manufacture. If, for example, the hairs of a skin are dissolved by chemical means or depilation is effected in any other way, and if, after thus removing the hair and washing the skins, they are placed in tanning material, leather would be formed, but it would certainly not be ideal, for from skins so treated the leather would be hard, brittle, thin and poor, and, consequently, useless for industrial purposes, because the foreign matters contained in the skins would combine within the fibers with the tanning material and thus make an inferior quality of leather. Even if these foreign matters were eliminated without taking care of other necessary processes, the defects above-mentioned would still exist to a

Digitized by Google

certain extent, although they would be much less pronounced. The defective relaxation of the fibers alone, and the imperfect opening of the pores within the skins will always produce to a certain extent the drawbacks just described.

As is well known, tanning materials have an astringent action; therefore, to allow the tannin to thoroughly penetrate hides or skins, it is necessary that it should have free access, and, if the process is to be carried out in the most effectual manner, foreign matters must be thoroughly eliminated from the skins so that the tanning ingredients can completely penetrate them and fill up the interstices between the fibers. If the tanning material cannot penetrate the skins because the pores are not sufficiently open, the fibers resist the action of the tannin and the tanning matters are deposited in small quantities on the first partially opened pores resulting in an empty, thin leather, poorly tanned and of little pliancy. Consequently, the foreign matters must be eliminated as no success can be obtained without a suitable relaxation of the internal structure of the skins. With the expansion of the fibers and the partial division of the connective tissue the interstices of the skins can be enlarged; their separation is thus facilitated and the necessary space is obtained for a sufficient deposit of the tanning agents. The opening up of the pores and of the internal cutaneous network of fibers is indispensable since the separation of the fibrous tissue of the skins permits a full and free introduction of the tanning material. These two matters form, in my opinion, the center of gravity of the tanning process, the other operations being secondary by comparison.

It is well to note as a general axiom that if the manipulation of the skins at these critical periods is at fault there is no remedy to repair the damage done, and the finished product will show these defects, often to the great surprise of the tanner. If, on the contrary, the operations of soaking, and particularly of liming, are carried out successfully the subsequent difficulties of working, with which the tanner is also faced, are largely modified, and the ultimate results will, as a rule, be satisfactory.

The consideration of the suitable strength and resistance of skins which next claim attention may appear to be unimportant, but it is agreed that the skin in its natural state, as it leaves the

Digitized by Google

animal, possesses the highest qualities in regard to the strength of its fibers. Every operation that must be given to skins in converting them into leather has a certain effect on this natural tenacity, so much so, in fact, that one could very well define the art of tanning as a process which ought to be carried out with the object of preserving the best possible amount of the natural strength of the skin. It is an indisputable fact that the more a skin is tanned the less is its resistant power and vice versa. But that is not to say that this effect cannot be accurately limited, and even reduced to a certain minimum. Some tanners believe, for instance, that by limiting the process of liming to just the time required to permit the removal of the hair the resistance of the skin is preserved. This is often a grave mistake. It is quite an easy matter with the aid of chemical means to loosen and remove the hair from skins in a few hours. But if such skins were submitted to the process of tanning the leather produced would not be tough and durable, but would be empty, brittle and of poor resistant qualities. The state of perfect tenacity cannot be obtained if the skins are not prepared in a suitable condition by submitting them to a useful and rational method of soaking and liming, in order to preserve their qualities and to permit a perfect conversion into leather. This quality cannot be obtained unless, in the process of liming, a relaxation of the fibers of the skins takes place by which the foreign substances they contain can be liberated and the interior structure thus rendered accessible for the tanning matter. On the other hand, the liming, while producing this necessary relaxation of the fibers, may act on other parts of the skin, and in order that this action is not allowed to exercise a destructive influence, it must be carefully regulated and limited to a certain point, because, when prolonged, the fibers of the skins would be exposed to the destructive action of the lime and would lose a great deal of their original tenacity. In verification of this theory, it is only necessary to state that raw pelts lack the power of assimilating the necessary amount of tanning matter, while skins which have been too strongly limed produce a soft and spongy leather. I will endeavor to show the happy medium that will exclude the danger of liming too much or too little, and shall have no difficulty in finding a system based on practical experience and one

Digitized by Google

which I have thoroughly examined, a system that each tanner must carry out and adapt to his special local conditions.

Resistance, flexibility, softness, and the consistency of leather, which are only recognized by the touch, are based on the exact relaxation of the fibers of the skins. If the fibers remain bound owing to insufficient relaxation, this alone will impart a harsh feel to the skin and if to this be added the loss of the active constituents of the tanning material, which have a filling action between the fibers and skins, and which ought to produce the necessary flexibility, it can easily be seen that the resultant leather will lack resistant power, *i. e.*, resistance in wear and general water-proof qualities. The same drawbacks are noticeable in leather tanned from hides whose fibers have been excessively relaxed; there is a serious loss of albuminous and gelatinous matters due to the prolonged action of lime, so that the skins have an empty, and sometimes hard feel of poor flexibility and wearing qualities. Body or fulness is that condition of the leather in which the fibers of the hides or skins have been perfectly fixed by the tanning materials used, and the property is easily recognized by the feel. Taking a transverse section of the hide it will be noticed that with correct liming the chief characteristics noticeable are smoothness, clearness, and no apparently horizontal layers or channeled fibers. This close and regular combination of the fibers cannot be produced, however, if they have not been changed from their natural condition. The natural condition of the fibrous network is disturbed by an excessive swelling in the limes. If this state of contortion reveals itself there is no possibility of reproducing the natural condition of the fibrous network in the hides; the foundation of the hides is thus lost without hope of regaining it, and a condition of emptiness and sponginess is shown in a transverse section of the hide. This condition is still more pronounced in flanks, the fibers of which are relaxed, fallen and without consistency. Leather insufficiently limed, and therefore not swollen and relaxed to the necessary degree, will also lack compactness, as such skins cannot absorb the necessary quantity of the tanning matter and will be defective, for such matters are lacking as ought to form an essential part of the finished product.

From these considerations it can therefore be easily under-

Digitized by Google

stood that the principal quality of a good leather, combining the properties of resistance, pliability and fullness, are to be ascribed to those features, and are due solely to an exact, opportune swelling and relaxation of the hide fibers by the process of liming. It is thus of paramount importance to every tanner that the process of liming be considered as one of the principal operations of tanning and one to which his best attention must be given.

I will now try with the help of my little experience to refer to the principles according to which the process of liming should be conducted in order to effect a proper swelling effect and relaxation of the skin and, first of all, the process will be considered in respect to its harmful action. The pungent odors of old limes are really only the ammoniacal vapors. But this ammonia in lime is, in my opinion, a very salutary factor among the substances found in used lime liquors because it is the natural mordant which rapidly penetrates the fibrous network of hides and skins, and prepares the way for the easier and more equal reception of the lime. Moreover, it has the effect of decreasing the causticity of the lime and thus permits a milder action of the latter substance. In a fresh lime liquor, in which ammonia has not yet been formed, because the necessary conditions, *i. e.*, animal matters, are still lacking, the raw hide swells disproportionately, because the mordant property of the lime, without the ammonia as a regulating factor, exercises all its action on the fibers. A hide or skin limed in this way has, when made into leather, a harsh and rough grain and little pliability.

Our predecessors, without knowing the reason, had a long time ago recognized this defect and preferred the old limes, and even prided themselves, when moving old liquors, on the extremely pungent odor produced by the ammoniacal vapors present, rather than make up a fresh lime liquor, although the expense of a new liquor was quite insignificant. Thus, without it being understood, the old empirical methods had established the axiom from practical experience that ammonia is a necessary adjunct to the successful working of lime liquors. First of all, therefore, the formation of a certain quantity of ammonia must not cause any alarm, but its production should be encouraged to a suitable extent.

Digitized by Google

In a new lime liquor the hides or skins can receive the beneficial effects of ammonia in two ways: (1) By adding to the freshly made lime liquor a small quantity of the old from the most backward pit or (2) By the addition of liquid ammonia. Some eminent scientists have expressed the same views, among whom are Professor Procter, Professor Eitner, and Villon. The latter has already described a method of unhairing directly by the use of ammonia, and in my experiments on a large scale as the director of a tannery I have been able to confirm its efficiency. According to Villon, unhairing with ammonia is one of the best methods, but perhaps too complicated, and the method of using it is especially difficult for workmen. The process is carried out in wooden vessels of about 1.50 meters diameter, and of a similar height. These are fitted with a lid 5 c. m. thickness. The vats, of which four or five are used, according to the size of the tannery, are each connected by a tube to a horizontal tube above, which unites them. Each communicating tube has a tap, while the discharge tubes are fitted in the lower part of the vats. Convinced that the use of ammonia will sooner or later be the object of serious study and practical research, I think it is interesting to note the quantity prescribed by Villon. For 1,500 kgs. of hides the following quantities are required:—

50 kgs. ammonium sulphate.
20 kgs. limed, slaked in 100 liters of water.
200 liters cold water.
665 grams ammonia per 100 kgs. of skins.

In the apparatus the ammonia is recovered with a loss of only 520 grams. As stated above, the use of this recipe is not practicable, but satisfactory results can be obtained by various modifications. It must not be forgotten that in the depilation by the use of alkalies, ammonia takes the third place as regards its effective strength, being preceded by caustic potash and caustic soda. The following table shows the results of a series of experiments carried out by Villon to test the relative efficiency of the alkalies for the process of depilation:—

Digitized by Google

	Weight of alkali used in 1,000 parts of water					
Alkali	1	2	5	10	20	25
Caustic potash	40	35	28	22	18	15
Caustic soda	50	45	37	30	27	22
Ammonia	58	53	48	29	24	20
	Number of hours required to remove the hair					

The results of Villon's experiments, also carried out with many other alkalies, show that:—

1. Depilation is only proportionate to the quantity of alkali used.

2. The more energetic the alkali the more rapid the depilation.

3. Alkalies, combined with metallic oxides, have weaker depilatory power than when they are free, and proportionately less if the oxide is not so strong.

4. Depilation is proportional to the temperature.

It will be asked—What are the dangerous effects produced by the use of too old lime liquors? The answer is: In the decomposition of the animal matters, which are always produced in the liming of hides and which lead to the formation of ammonia. The more hides and skins are treated in these liquors so much greater is the quantity of ammonia formed, by which the lime certainly exercises a milder effect, so that the limed skins come out much softer from such liquors. But it is not necessary nor desirable to carry this treatment too far, because once the formation of ammonia is carried to a certain useful point, it is decidedly dangerous when that point is passed. The free ammonia has then a damaging and destructive action, because the ammoniacal salts accumulate, and not only have these salts a loosening action on the albuminous matter, but also, if the action is prolonged, a very destructive effect on the fibrous tissues, for all of these organic matters would eventually putrefy, by which the ruin of the hide or skin would be complete. Therefore, the more the ammoniacal salts collect in a lime liquor so much greater is the danger of spoiling the hides. These ammoniacal salts or, as it would be better to term them, products of putrefaction originate from the hides themselves, from the blood, albumen, or humors and impurities arising from the hides. The quantity of these ammoniacal salts is increased by every new lot introduced, while the season and relative temperature have a

Digitized by Google

considerable influence. The warmer the lime liquors the quicker the action or transformation, and vice versa, for it is well-known that heat favors putrefaction. Nevertheless, it must not be overlooked that fresh lime has some years ago been shown to be an antiseptic or rather an antidote against putrefaction; and if the lime liquors be always strengthened with fresh lime, and provided that this strengthening be done in time, a putrefactive action cannot be produced. The fact must not be lost sight of, however, that animal matters enter very quickly into the process of putrefaction, especially if the temperature is rather warm. Therefore, if it happened that an excessive putrefaction took place at the conclusion of the process, it would appear that the quantity of lime calculated for that particular lot could not have been sufficient to completely neutralize the putrid gases which were formed. In other words, it means that the lime liquors must receive careful study and judgment. It must always be remembered that, after the removal of a pack of hides or skins from a lime liquor, an excess of these ammoniacal salts is left behind. Now, if this accumulation has become so heavy that, after a few days, the lime is subject to this reaction, the destructive effect of the lime liquor shows itself and attacks with great force first the more gelatinous matter and adipose tissues of the hides, next the flanks, then the grain and finally the innermost fibers of the corium or true skin.

This incipient state of putrefaction in hides is recognized by their spongy and viscid appearance and slippery feel both on the flesh and grain sides; dark yellowish opaque spots appear on the grain, and when the hides are in an advanced state of decomposition these blemishes are changed into a greyish-back coloration. Finally, the hides may be broken over the whole of their surface, so that when every part is damaged and partially destroyed, the hides often fall to pieces.

These destructive effects are arrested, but not remedied, by the addition of a larger quantity of fresh line, which should always be added at shorter intervals; or, better still, as soon as the first symptoms of putrefaction are noticed, transfer the hides to a new lime liquor, where the production of the necessary quantity of ammonia can be regulated to the average content in a used lime liquor. It is somewhat difficult to determine precisely what

Digitized by Google

the average amount of ammonia in early lime liquors ought to be, because no definite general rule has been established. In this instance the tanner is limited to the usual practical data, and must trust to his own careful observations to ascertain the maximum effect that the ammonia has in checking the swelling of the fibers. If too little ammonia is added to a fresh lime liquor the drawbacks of excessive swelling quickly show themselves, while, if the addition has been too strong, it has soon the worst effect that can possibly happen, even to the extent of destroying the hides. This naturally raises the question as to what ought to be done to arrive at the correct method of carrying out this particular process of liming, in which so many troublesome and dangerous combinations enter and how to decide on a process by which hides can be unhaired without difficulty and yet possess the right degree of relaxation so far as the fibrous tissue is concerned. A very suitable reply would be that "it all depends." The reply seems to me to have been given in my preceding remarks.

Usually the system of liming necessary is one supported by experience, well thought out and arranged and correct in detail. Each tanner should do this for himself, for the process must be adapted to special local conditions, such as the quality of the lime, the water, and the temperature. It is quite impossible to give prescriptions or fixed certain methods that would be universally practicable. A certain latitude must be allowed to every practical method that will lead to the establishment of a perfect process, and which the tanner himself ought to observe, intuitively acquiring the faculty of determining when the exact moment comes for removing the skins from the lime liquor. The following conditions should therefore be duly noted:—(1) The duration of the liming process; (2) the strength of the lime; (3) the nature of the water; (4) the content of ammonia (which will depend on the age of the lime liquor); (5) the number of hides in relation to their weight; (6) their quality; (7) their origin; (8) their previous condition or state of preservation, whether fresh, salted, dry salted, dried or arsenicated, etc.; and (9) the season of the year and the temperature of the liquors. The length of time taken by the process must be determined and the rational system of liming regulated solely according to the quality

Digitized by Google

of the hides or skins, the quality of the water, and the prevailing temperature.

Hides should also be sorted, if of varying qualities and be treated in the limes accordingly. Where this sorting is not carried out or is done improperly it is impossible to get a completely satisfactory result in the liming process. The hides or skins should be sorted into three grades—light, medium, and heavy—at least, but it would be even better if they were more closely classified to secure perfectly uniform results. Young hides should also be separated from the old as they require different treatment. With hides thus assorted the tanner ought to have no difficulty in quickly finding the exact standard of treatment *i. e.,* how much time is required for light hides how much for heavy, and so on for each class of hides or skins treated so that they be sufficiently relaxed and limed. Complementary to these observations it may be remarked that the hide in its normal state regulates itself, as it were, in the process of liming, but it is necessary to find the exact treatment, according to their requirements, of hides in an abnormal condition; that is why a classification is necessary to arrive at a rational method of liming.

The strength of the lime liquors plays only a secondary part in the process, since one of the principal physical properties of lime is its limited solubility in water; in fact, it is known how indifferent and peculiar is the action of lime, for, besides its limited solubility, it is actually more soluble in cold than in warm water. That is why it is so difficult, if not impossible, to make lime liquors stronger or weaker. The solubility of lime has been frequently the object of chemical research, but the figures determined by different chemists do not always agree. The following table of the determinations of the solubility of lime was compiled by Mr. H. Guthrie, and is probably one of the most accurate.

The expression "a strong lime liquor" has, therefore, no real meaning. It should rather be described as an over-loaded lime liquor, and one charged more or less with ammoniacal salts, because the action of the lime in its varied liquors arises principally from its combination with nitrogen which then forms putrefactive products, *i. e.*, ammoniacal salts, the production of which

Digitized by Google

100 CC. OF A SATURATED SOLUTION OF LIME.

At	5	degs. C.	contains	0.1350	gr. CaO
"	10	"	"	0.1342	"
"	15	"	"	0.1320	"
"	20	"	"	0.1293	"
"	25	"	"	0.1254	"
"	30	"	"	0.1219	"
"	35	"	"	0.1161	"
"	40	"	"	0.1119	"
"	50	"	"	0.0981	"
"	60	"	"	0.0879	"
"	70	"	"	0.0781	"
"	80	"	"	0.0740	"
"	90	"	"	0.0696	"
"	100	"	"	0.0597	"

must be carefully regulated, because by the too prolonged influence of these products the fibers of the hides are loosened too much, as shown by their flabby and spongy nature. The action of pure lime, whether in small or large quantities, is antiseptic, and is not sufficiently strong chemically to seriously damage the hides. It acts on albuminous bodies, but only moderately, bringing them into a condition of incipient solution without depriving the skins of albumen, and simply rendering them capable of absorbing larger quantities of water. These important facts were confirmed by Davy's experiments, which are worth recording.

First Experiment.

August 27, 1829.—Various portions of animal substances in such a state of incipient putrefaction as to emit a fœtid odor were immersed in lime, put in a vessel and hermetically sealed, being, therefore, without contact with air.

September 27, 1829.—Pieces examined; found in an excellent state of preservation; swollen, but the delicate fibrous structure was neither corroded nor damaged.

May 27, 1829 (after nine months' immersion).—Examined again; found in similar condition, and with the fibrous structure quite intact in every part.

Two years Later.—A considerable change had taken place. The cuticle had become soft and transparent, and many parts of the fibrous network were indistinct.

Digitized by Google

SECOND EXPERIMENT.

Six Months' Test.—Skins were placed in lime in á suitable receptacle. When opened at the end of six months there was no putrefaction, only a strong smell of ammonia. The skins submitted to the action of lime were found to be well preserved, except that the greasy matters contained in the cellular tissues had become opaque, bleached, and saponified by the alkalinity of the ammonia. After many other experiments, the famous chemist came to the following conclusions:—

"After animal substances are subjected to the action of lime they cease to become putrescible; they resist putrefaction better if protected from the air or immersed and kept in water. Lime does not exercise a destructive effect on animal substances, nor promote their decomposition, but on the contrary it has a strongly preservative and decidedly antiseptic power, which arrests putrefaction even when it has previously been well advanced."

The laws laid down by Davy can be suitably applied to the practical management of the process of liming. On the basis of the results recorded above, the strong swelling effect on skins in a solution of pure lime can be readily understood, and it is most important that this swelling effect should be checked at the psychological moment. All those substances which restrain this strong swelling effect when added to lime liquors are, therefore, recommended and fortunately, there are many such substances at the disposal of the tanner. If due attention is not paid to this matter the internal structure of the hides or skins is affected by the strong swelling action with the disastrous consequences that have just been described. Among the bodies that arrest excessive swelling are, as I have already noted, the ammoniacal salts. The addition of magnesium carbonate or China clay to lime liquors that are too fresh has also a mild action and restrains the swelling of the hide. So far as is yet known, the exact content of ammonia in limes has not been established either by volume or weight, but what I would particularly like to impress upon the students at this school is that the use of ammonia in the leather industry has a great future, and I commend the study of its best application, particularly to the process of preparing hides for unhairing.

Digitized by Google

Referring to the dose of ammonia in lime liquors, I would like to point out that excess in that process also shows itself in the process of tanning. This surplus is at once recognized if the lime liquor liberates free ammonia, which is characterized by its pungent odor that sometimes causes the workman moving the liquors to gasp for breath. On the other hand, an insufficient quantity is more difficult to determine during the process, but this defect is usually recognized in practice by the excessive swelling of the skins in the limes, and later by the difficulty found in removing the hair, and especially the fine, short hairs underneath, while the edges of the skins are irregular in shape and appear to be contracted. To find the happy medium and the safety point when the ammonia should be controlled, we must still resort to empirical methods. The quantity of skins to be limed ought to be taken into consideration in a well regulated method, because the action varies considerably according to the quantity. As already noted, the ammoniacal salts, products of putrefaction, are formed from the blood, humors, impurities, and albuminous bodies yielded by the skins to the liquors during the process of liming. Now it is a natural corollary that the greater the quantity of skins yielding these materials the more the products of putrefaction in the lime liquors. To keep the process of liming always uniform, the same quantity of skins of corresponding weight must be regularly worked through, because only in that way can the tanner be assured that at a certain time the right quantity of ammonia will be formed.

In a new lime liquor made with pure lime there are neither ammoniacal salts nor products of putrefaction, and it is only after a pack of hides have been treated that these develop in the way I have described. Therefore, there is no real danger in this direction in regard to the first pack passed through a freshly-made lime liquor. Neither is there much to fear in the second pack treated in the same liquor, for the process of the formation of putrefaction is not yet sufficiently active to exercise a destructive action. In the third lot, however, there are frequently signs of putrefaction in the limed hides; thus for every successive pack in this same liquor the danger increases, so that if its use is prolonged, it is easy to understand that the excessively putrid condition of the liquor will eventually ruin the hides.

Digitized by Google

unless freshly-slaked lime is added to neutralize the deleterious action of the putrefactive elements. In this case, however old the lime liquor may have become, the addition of fresh lime in increasing quantities at shorter intervals will restrain the too active effects of the products of putrefaction.

Nevertheless, a safe process of liming is not possible by this method, as we have seen, and therefore it is better to use the same lime liquor only three times, and to carry out the process in a series of three lime pits, by which system there is nothing to fear. A lime liquor after being used three times should be thrown away and a fresh liquor substituted. A regular system of liming is thus established that cannot fail to give satisfactory results. The origin and class of the raw hides is important in the process of liming, in that the various hides which come from different parts of the world do not absorb the water and lime in the same way—for example, hides from torrid climes are more difficult to soak than those from temperate regions. There is also the age of the hides or skins to be considered, since old hides are, as a rule, less sensible to the action of lime liquors than hides from young cattle. In all the processes of soaking, whether in water or chemical solutions or stale liquors, the smaller as well as the larger hides can be treated in the same way and under the same conditions; at least, the advantages of classifying the hides for this process are quite insignificant. Some soaking processes, perhaps, are conducted solely according to the age of the animal, the condition of dryness, the time the hides have been in the hair, the state of preservation, time in warehouse, and the season when put into work; other regulating factors may be the substance, the length of hair, and the method of salting.

Two principal selections are made in liming calf skins, viz., the skins of milk calves and of the grass-fed. These act very differently in the liming process, the former requiring much less time than the latter. A similar division of treatment is also necessary for other qualities of skins. The temperature of the lime liquors must be constantly maintained. In summer they should be kept at the temperature of the surrounding atmosphere, and in winter, if the temperature falls below 10 degrees C., it must be increased to 15—20 degrees. Warmth exercises a great influence on the liming process. It is true that the solu-

Digitized by Google

bility of the lime is lessened by increasing the temperature, but the action of the liquor is quickened. At too low a temperature (under 10 degrees C.) the lime liquor completely loses its action. A medium temperature of 15—20 degrees C. is the best.

Let us now carefully recapitulate the essential points of the liming process:—We must not allow the liquors to develop too much ammonia, leucic acid, caproic acid and tyrosin, bodies which precipitate gelatine; it must be observed that in the cold season the bacteria do not multiply so rapidly; attention ought to be paid to prevent the formation of spherical concretions of calcium carbonate or chalk; liquors should not be allowed to putrefy, as although such liquors facilitate and hasten depilation, the structure of the hides is endangered.

Only by observing these details shall we thoroughly understand the process of liming, and that lime is not really a dangerous material to use. As a famous scientist beyond the Alps has remarked, it is the depilatory par excellence. Personally, I have found it the best depilitant either used alone or in combination with other materials, and I hope to discuss the special features of combined depilatory liquors in another lecture.

CHROME SOLE LEATHER.*

Those connected with the leather trade for the past decade or so are conversant with two predictions in regard to chrome sole leather. The first of these predictions that of the imaginative enthusiast, who may or may not have had practical experience in tanning the leather, is that it is only a question of a few years when bark-tanned sole leather will be like alum tanned kid at least for shoe purposes a thing of the past. Strange this prediction was just about as current ten or fifteen years ago as it is to-day. Because the prospects of the realization of this prediction are apparently just about as remote to-day as they were ten or fifteen years ago, the negative prediction about chrome sole that it never will amount to much of anything is also just about as frequent as it was ten or fifteen years ago. There is this much, however, to be said for this latter negative opinion when as fifteen years ago it was simply from sheer conservatism,

* Editorial, *Shoe and Leather Reporter*, Sept. 19, 1912.

Digitized by Google

to-day so little apparent progress has been made that evidence seems to justify it. Yet there are signs that the casual observer may overlook which indicate the era of chrome sole is nearer than we think. Or perhaps it would be more correct to say that while neither of the predictions in regard to chrome sole leather are completely true, yet both have elements of truth.

So far as the probability of a chrome sole being produced that will have the physical properties of present vegetable tanned sole leather we are frankly skeptical. A piece of sole leather well tanned by vegetable materials, that is not unduly swelled by acid or burned by bleaching, represents a combination of a number of desirable physical properties. It has departed very materially from its original hide nature. It has become a material which is comparatively hard and rigid, yet it is tough and moderately flexible. These properties make this leather particularly suited for soles of a certain class of shoes, but it does not necessarily follow that the properties this vegetable tanned sole leather possesses makes it desirable for all classes of footwear. Indeed, to us it seems quite reasonable that for many classes of footwear a material might be more desirable than this leather and an evidence of the correctness of this view is the enormous demand for sneakers and other rubber-soled shoes.

We believe one great retarding influence in the development of chrome sole has been the desire to duplicate a bark tanned sole instead of developing the chrome sole on its merits. It is true that much ingenuity has been spent on devising fillers for chrome soles, but here let us emphasize the essential difference between the chrome leather and the vegetable tanned; one hundred pounds of the latter contains on the average of 45 pounds of hide substance, 45 pounds tannin and 10 pounds of oil, moisture, etc., while the chrome leather without filling contains 90 pounds hide substance, 5 pounds of chromium oxide and 5 pounds oil, etc. In other words, the ratio of tannin to hide in the vegetable-tanned leather is 1 to 1, while in the chrome it is about 1 to 18, indeed it probably could be 1 to 30 without making a material difference.

It is true that the chrome sole leather can be filled, but so in a large measure can the bark-tanned leather be filled, but when you begin to fill you depart from the nature of the leather; that

Digitized by Google

is, there is this difference that the tannin is in a measure chemically combined with the hide substance, but the filling is simply a mechanical absorption. To show the possibilities of the chrome sole per se a shoe manufacturer in a neighboring city bought up a lot of light chrome-tanned sole very slightly filled, sewed a sole from two thicknesses and put it on a low-priced upper for a children's play shoe. The store that has had these shoes on sale has had no widespread advertising campaign. The question has simply been to keep the sizes in stock and it appears from some of the sizes demanded that pretty large children appreciate a good-wearing soft-soled shoe. So in general it is safe to predict a large future for a chrome sole which will not be so heavily filled as to resemble an oak sole, but which will have a little body and at the same time the wear resisting properties and imperviousness which make chrome leather so valuable

---

THE FRENCH GOVERNMENT AND CHROME LEATHER.*

The French Government has issued certain regulations with regard to the supply of chrome leather for military purposes, and apart from the effect the conditions of supply may have on French chrome leather manufacturers the subject is not without general interest to the leather trade. Briefly, the regulations include a clause which places a ban on chrome leather made by the two-bath process for military purposes. The main objection to this class of leather appears to be that it contains a certain amount of free sulphur, though it is not clearly explained why the presence of this by-product of the chrome process is injurious; but judging by the very strong protest which has been submitted to the Government authorities by the French manufacturers of chrome leather, it would seem that the complaint was implied, if not actually made, that the wearing qualities of the two-bath chrome leather are impaired by the presence of free sulphur. To prove that there is no foundation for the belief that the strength of such leather is inferior to that made by the one-bath process, the French tanners who have largely centered their attention on the two-bath method, sent with their note of protest

* *Leather Trades Review*, Oct. 2, 1912, Editorial.

Digitized by Google

several pieces of chrome leather containing over 5 per cent. of free sulphur. These pieces had been cut off some tire covers which had stood the wear and tear of a 4,000 miles journey attached to motor-car wheels, and were little the worse for the test. So far, so good. The manufacturers were quite justified in calling the attention of the authorities to the matter, if it were simply a question of wear, for if the chroming by the two-bath process is carried out in a scientific manner, and if too much acid is not used, there is no danger of the fibers being weakened in any way. On the other hand, the claim that chrome leather produced by the two-bath process is much stronger and more durable than that made by the single-bath can scarcely be substantiated by general experience, and it would be difficult to support the French chrome leather manufacturers in this assertion; neither can it be affirmed that the double-bath method is more under control than the other process, a theory that has been advanced in this particular case in furthering the claims of the French manufacturers that the Government ban on the two-bath chromed leather should be removed As a matter of fact, the one-bath process is much easier of application, and a slight overdose of the leather-making liquor has no serious results, while it must be acknowledged that the two-bath method requires very great care and a certain amount of scientific knowledge to regulate the strength of the liquors, and to apportion correctly the solutions that go to make up the two baths.

Taking an unprejudiced view of the relative merits of the two processes, it must be admitted that both have special and particular advantages for the manufacture of certain kinds of leather, and there is probably quite as much leather made by the one-bath method as by the two-bath, which is apparently so much favored by French dressers. Where the leather is required to be specially pliable and mellow on grain, and the skins must be kept as plump as possible, the double-bath process is undoubtedly superior, and that is why the process is so much favored in the making of shoe leathers, such as glazed kid and calf. The method is also adapted for natural chrome leather, especially when the latter is required to be finished white, or nearly so. In fact, the Americans can produce almost a perfect white calf leather by the process, adding a certain proportion of alum,

Digitized by Google

salt and flour, but, strange to say, this leather does not appear to be made by British tanners, although there is some demand for it in this country. Possibly, too, the two-bath process is better adapted for leather used in the making of motor tire covers owing to its greater resiliency and the ease with which it can be vulcanized on rubber.

In the case of belting, however, the one-bath chrome leathers appear to have a decided advantage, as they do not stretch nearly so much as those produced by the double-bath method. Thousands of dozens of box and willow sides are also successfully made by the use of one-liquor, and, of course, for chroming leather that has already been tanned, *i. e.*, for the process known as combination, or semi-chrome, the one-bath liquors are exclusively used.

It is quite likely that the French Government authorities have been advised by their experts to discard the buying of chrome military leather containing free sulphur in favor of the single-bath leather for other reasons than that of weaker tensile strength, which, as mentioned above, is a debatable point, and is not confirmed by general experience. For instance, if the leather used for the special military equipment has to come in contact with any metal fittings, the latter would most certainly be tarnished and spoiled by the presence of free sulphur. In fact, a simple test often used for distinguishing whether a chrome leather has been made by the one or two-bath process consists in wrapping up a silver coin in a piece of the leather, and allowing it to remain there for a few hours, when the coin will be darkened by the two-bath leather and unaffected by the chrome leather dressed by the one-bath process. Where chrome leathers are used for ladies' and men's belts for ordinary wear this inconvenience can, of course, be overcome by the use of leather-covered buckels, but it can scarcely be expected that the same procedure can be applied to the manufacture of military belts. The sulphur content of the French chrome leather appears, however, to be abnormally high. With a thorough washing of the leather after chroming and previous to dressing there should not be more than 2 to 3 per cent. of free sulphur.

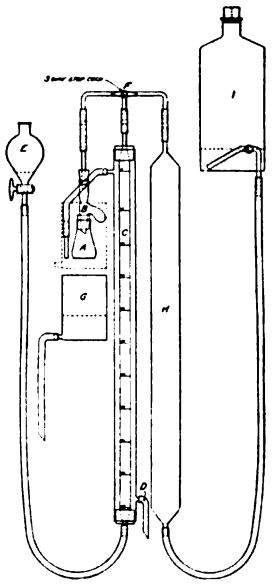
Whatever the outcome of the ministerial decree, the French leather dressers will have the exclusive privilege of supplying the leather required for all Government contracts, and, as they

Digitized by Google

are successful in the production of the two-bath chrome leather, they will probably have very little difficulty with the simpler one-bath process, if leather containing sulphur remains under the ban of the French Government. Only, it will mean some inconvenience in working the two processes in one tannery.

ABSTRACTS.

The Calcium Carbid Method for Determining Moisture. H. C. McNeil. Circular 97, U. S. Bureau of Chemistry. Calcium carbid was used as early as 1897 by P. Yvon for dehydrating absolute alcohol. Several investigators since have applied it for determining moisture in oils, butter, etc. The apparatus used by Mr. McNeil is shown in the figure.



The material to be analyzed is weighed into the flask *A*, 25 cc. capacity. *B* is the carbid tube, with a projection on one side holding 5-10 g. of carbid. *C* is a 100 cc. burette drawn out at the ends to facilitate connections. It is jacketed, and the jacket connected to the tap *D*, for rapid cooling and control of temperature. *E* is the leveling vessel. The liquid used in *C* and *E* may be mercury or a concentrated salt solution which has stood in contact with acetylene until saturated, and is colored with phenolphthalein and NaOH. If the substance is not a powder, add powdered SiO_2 or $BaSO_4$ and fine sand and mix until the whole is a dry

Digitized by Google

powder, so that the carbid can be brought into contact with all parts of the original material. Or, the sample may be dissolved or suspended in a suitable liquid, and treated with the carbid in this form. The carbid is ground to a fine powder and the projection of tube *B* filled with it. Then place a cotton plug in the vertical part of *B* above the projection, sprinkle some carbid on it, place another plug, more carbid, and so on till the tube is filled. This is to prevent escape of moisture in the form of vapor caused by the heat of the reaction. *B* is then connected with *C* and *A* with *B* by means of rubber stoppers, tubing, etc., as shown in the cut. Open the 3-way cock *F* to the air by pulling it out. Bring the vessel *G* up so as to surround *A*. Allow tap water to flow through *C* into *G*. When the temperature of the whole is brought to that of the tap water, bring the liquid in *C* to the zero, turn *F* so that *A* and *B* communicate with *C*. Lower *G* and tip *A* so as to spill a little carbid into it. The rate of reaction is controlled by the rate of admission of the carbid. When all the carbid has been introduced and thoroughly mixed with the contents of *A*, place a vessel of water in the place formerly occupied by *G*, and boil it 10 or 15 minutes or as long as gas continues to be generated. A glycerin bath may be used, thus making a temperature of 130° C. possible. *E* should be lowered as the reaction proceeds, so as to keep the liquid level in *C* and *E* nearly the same.

When the reaction is complete, remove the water-bath, replace *G*, and when the temperature is again the same as at the beginning, read the volume and temperature and reduce to standard conditions. The temperature is read by a thermometer in *G*.

The tube *H* is an auxiliary container for use when the substance has a large proportion of moisture, or is of such a nature that a fair sample of small size cannot be taken. In such a case *F* is so turned that both *C* and *H* communicate with *A* during the reaction. Then by changing the position of *I*, separate portions of the gas in *H* may be forced into *C*, cooled, measured and expelled. In order to calculate results, it is necessary to know how much gas a known quantity of water generates. This should be determined under conditions as nearly as possible the same as those of the moisture determinations. In practice 1 gram of water usually gives about 580 cc. of acetylene.

The author has used the method for determining moisture in paint, paint materials and soaps. Many liquids were examined with reference to their availability as solvents for substances not easily powdered. Toluene does well for most paint vehicles. Alcohol which has been treated with calcium carbid, so as to be dehydrated and saturated with acetylene may be used. Amyl alcohol may also be used, and in some cases anilin oil. In general the dry process gives better results, and the author prefers that whenever it is practicable. The process has been applied to various infants' foods, and milk sugar, and proved very slow in operation. Determinations on flour, leather powder (both vegetable and chrome tanned) and sawdust have given good results.

Digitized by Google

Western Hemlock. U. S. Dept. of Agriculture Leaflet. The wood of this species (Tsuga heterophylla) is better than that of the eastern hemlock (Tsuga Canadensis), being suitable for flooring, siding, etc., as well as for joists, etc. It is also suitable for paper pulp. The bark contains from 10 to 20 per cent. tannin, and is beginning to be utilized. This hemlock grows in damp localities from Prince William Sound Alaska (Lat. 60°), to the Golden Gate (Lat. 38°), along the Pacific coast, and inland as far as the western spurs of the Rockies. In Washington the finest trees grow at altitudes from 2,000 to 3,500 feet, on slopes where the annual rainfall is 70 inches or more. It grows in association with the Douglas fir, and with the western white pine. It can endure heavy shade, growing very slowly under these conditions, and when air and light are admitted recovers rapidly from suppression. It suffers from fire, even surface fires sometimes destroying a stand, because its bark is not thick compared with other trees of the same region, and its roots grow near the surface. It is also subject to injury from fungus growths.

Myrobalans. C. M. Procter. *S. & L. Rep.*, Sept. 19, 1912. Myrobalans are the fruit of several species of Terminalia, growing in India, chiefly Terminalia chebula. This tree grows from 25 to 50 feet high. The nuts are gathered in the fall, some being picked from the trees green and others shaken down. After being gathered they are spread out to dry on suitable areas of rock or earth. The different districts from which the nuts come give the trade names to the varieties, Bhimleys, Jubblepores, etc. Each kind is sorted into three grades, "picked," "No. 1," and "No. 2." The picked nuts average lower in tannin than the No. 1, but are lighter in color. The percentage of tannin varies from 25 to 40, most of it being in the husk. The nuts may be leached whole to very good advantage. Myrobalan liquors are good acid-makers, because of the large percentage of fermentable non-tans. Bhimley nuts are the best for acid making, while Jubblepores are better for bloom and weight-giving properties. Myrobalans tend to lighten the color of most tannages. They cannot be used to advantage in larger proportion than 30 per cent. of the total tanning units.

Popular Illusions in Regard to Tanning. Alan A. Claflin. *S. & L. Rep.*, Sept. 19, 1912. It is popularly supposed that the leather of past generations was better than that made to-day. It is true that by the wasteful use of oak-bark our ancestors made excellent sole-leather and wasted much time in making it. For a very large proportion of the time there was absolutely no tanning action taking place, the hides simply remaining in liquors from which the tannin value had long since been absorbed. Leather is made primarily from a natural product, the hides and skins of animals. It depends for its strength in the first instance on the strength of the hide-fiber. The function of tanning is to preserve the strength of this fiber, not to create strength for it. What the chemist

Digitized by Google

can do and is doing is to prevent the use of tanning materials and processes which damage the natural fiber of the leather. Our best leather is now of very high quality and it probably is impossible to improve on it a great deal; the trouble is that the best leather is too infrequent. The work of the chemist is to so systematize tannery practice that good results may be duplicated. When this is completely accomplished tanning will be on an absolutely scientific basis, and it is much nearer that to-day than most of us realize.

Drum-Tanned Leather. *S. & L. Rep.*, Sept. 19. 1912. In the process of tanning heavy leather with extracts in drums it is advisable to thoroughly delime the hides with lactic or other acid and then to start the tanning by suspending the hides in liquors which should be kept constantly agitated. The first two or three liquors should be just strong enough to remove the last traces of lime and also to keep up the substance of the hides. After the suspenders, the hides should be folded and placed in the drum for the more rapid tanning with strong liquors. The best extracts rapidly penetrate the hides and do not make the grain of the leather harsh and rough. Sulphited extracts produce the best results in drum tanning. For pliable leather quebracho extract is very satisfactory, but it does not produce sufficient firmness for sole leather unless it is combined with other extracts.

Chestnut extract is the most satisfactory extract to use alone in drum tanning; it also works well in combination with other tans. Handling the tanned leather for a few hours in weak sumac liquor is an excellent way to remove the extract from the grain and flesh without injury to the weight of the leather by disturbing the tan in the interior of the stock. Drum-tanned leather should be dried without sun or wind or the color will be bad. Rolling the stock before it has been thoroughly dried out also injures the appearance of the leather. A hot air drying system is much superior to steam pipes and natural air. With such a system drum leather dries much faster than vat leather and there is less danger of mold. For oiling drum-tanned sole leather a mixture of three parts of cod and one part mineral oil is recommended. Drum leather dried with too much heat has a rough grain and will crack more easily than leather dried on ordinary heat of from 75 to 100 degrees.

Buffalo Robes. *Kansas City Journal*, through *Hide and Leather*. There was a time when Kansas furnished buffalo robes for the world. No well-regulated family on an eastern farm was without one. They were not only very warm but reasonable in price.

It was the Kaw Indians who first marketed buffalo robes. Later, manufacturers, seeing the vast profit in them, made them by the thousands and supplied the world. But the manufactured or patent tanned robes didn't last as long as the robes tanned by the Indians. In fact, it is said that the robes now in service were those tanned by these Indians many

Digitized by Google

years before the white men began to tan them. The Indian women did the tanning. They fastened the green hides to a set of frames just like grandmother used to fasten the quilts to when she made them. The squaws would then take a blunt implement, resembling a hoe, and work off all the flesh and membrane from the hide. Then they would rub the skin for several days with a heavy, smooth-surfaced club until all the grease had been driven out of the hide. They used no chemicals at all in tanning. Only hides from buffaloes killed late in the winter were used in making robes, as the fur was then heaviest.

Mocha Leather. *Leather World.* In a recent patent M. Jirovsky, of Berlin, describes a process for the manufacture of mocha leather in five or six days, instead of the lengthy process which is usually employed. The method is, briefly, as follows: The skins are first softened by soaking in water, and are then immersed in a bath made by adding 250 kilos of lime and 5 kilos of potassium carbonate to 400 liters of water, and which has been allowed to stand for twelve hours. The skins are immersed for three days, then unhaired, rinsed in tepid water, then put back in the first bath for five to six hours, again washed in water, and dipped in a solution of nitric acid made by dissolving 300 grams of concentrated nitric acid in 100 liters of water, then washed in water, smoothened, and immersed in a 1 per cent. solution of borax at 20° C., taken out, allowed to drain, and finished. The whole process thus takes only five or six days.

Lime Soap. *Hide and Leather,* Oct. 5. The white coating that appears on leather articles used in the beamhouse such as leather boots, aprons, etc., is caused by an insoluble lime soap. This coating appears on the goods after a few days' used and no matter how much care is given the articles such as a thorough washing every night, the coating is there just the same. If the articles have been made of leather that has been stuffed with tallow, fish oil, stearine, etc., as is usually the case, as soon as they come in contact with lime, a soap is formed that is insoluble in water and the result is that the leather will again absorb water in proportion to the amount of grease that is so changed to soap. It is a common practice for beamhouse workmen to take their wet boots, aprons, etc., and hang them up to dry near stoves or steam pipes. The result is hard and brittle articles. Regreasing is of but little use because the new grease cannot penetrate far into the fibers and is quickly saponified by the lime, leaving the articles in worse condition than before, and adding to their weight. The trouble may be avoided by using leather stuffed with non-saponifiable oils, such as paraffine and vaseline. These should be applied hot and the leather should be warmed also. The extra cost of this stuffing would result in the greater durability of the goods and far more convenience for the workman.

Digitized by Google

Pigskin Leather. *Hide and Leather,* Oct. 5. Hog skins make a fine seat leather for saddles. It is very porous, made so by the coarse hair and bristles which penetrate clear through the hide. Unlike any other hide, the hair pits go clear through from grain side to flesh, and this allows the air to pass through, keeping the saddle seat cool while riding. It is used to make pocketbooks. When finished, it is handsome and wears well. It is also used to make shoe counters, and it is said that for a medium-priced shoe it wears and works fine, being somewhat cheaper, also, than a shoe counter made of sole leather. When pigskins were first used in the manufacture of shoes, it was difficult to get all of the grease out of the skins, but, as it was used for insoles in the cheap shoes, appearances did not count for much. There were numerous complaints that, when the heat of the foot made the pigskin warm, the grease came out and ruined hosiery, besides emitting an unpleasant odor. This caused the tanner to be more careful to eliminate all the grease from the leather. The bristles go through the hide, and when the tanner neglected to shave them off close to the surface, they caused great discomfort to the wearer of the shoes. After the tanners rectified that fault, they began making better leather of the hog skins, and now it is used for making heels for shoes, and a slip sole for light shoes.

Since leather welting prices have gone so high, a pigskin welting is made for use in medium-priced goods, which seems to give satisfaction. It is being used in all kinds of leather novelty goods, as well as in gloves, so that it brings as high as 24 cents a pound, making it nearly as high as sole leather made from good cattle hides. Many fine shoes have pigskin box toes, and these wear well and are light in weight.

Russian Tanning Industry. Consul General John H. Snodgrass. *Daily Consular and Trade Reports.* The tanners are alarmed because the use of top-boots by the army is to be discontinued. Prices of raw material are rapidly rising.

Detection of Sulphite-Cellulose Extract in Leather. Dr. A. Gansser. *Collegium,* No. 509, p. 482. Procter and Hirst's anilin reaction for lignin has been recommended for the detection of sulphite-cellulose in tanning extracts. Beside the use of this material as an ingredient of tanning extracts, there is a large field for its employment as a substitute for other materials in the tannery, and so it becomes a matter of interest to determine whether the Procter and Hirst reaction can be used to detect the so-called "cellulose pitch" in the leather itself. For this purpose pieces of cowhide were tanned with extract liquors so made up that in one case 5 per cent. of all the extract used was sulphite cellulose, and in another 2 per cent. The finished leather was pulverized, and 30 g. of it shaken for 3 hours with 90 cc. of water at 40° C. The solution was filtered and diluted with 70 cc. distilled water to the color intensity of a 1.2 per cent. tanning solution. Fifty cc. of this solution were treated

Digitized by Google

with 5 cc. anilin and then with 20 cc. strong HCl. While a blank determination showed no cloudiness after a long time, the 5 per cent. sulphite cellulose leather extract showed the characteristic flocculence at once, and the other after a few minutes. L. B.

A Simplification in the Estimation of Nitrogen. R. NEUMANN. *Chem. Ztg.*, **1912**, p. 613. Klinkerfues (*Chem. Ztg.*, 1911, p. 1274) observed that the receiver into which the NH_3 is distilled over in the Kjeldahl process might by water cooling be made to retain an excess of NH_3. He therefore proposed always to use in the receiver less than enough standard acid to neutralize the ammonia, and to titrate the excess of ammonia with standard acid, thus avoiding the use of a standard alkali solution. Neumann found serious difficulty with this process when NH_4 salts were decomposed in test experiments, the results being from 0.1 to 0.2 per cent. too low. Similar results were obtained with other materials, such as bone meal. By the use of a properly selected indicator, he found it possible to get good results in all cases except the salts of NH_4. The best indicators are von Puschel's and Mohr's tinctures of litmus, the latter being preferable because it is easier to prepare. In the case of ammonium salts, however, cochineal gives the best results, and it is necessary to apply a correction, multiplying the quantity of acid used by 0.976. Neumann extends Klinkerfues' method by dispensing entirely with the preliminary quantity of acid in the receiver, simply catching the NH_3 in cold water. L. A. C.

Process of Decolorizing and Clarifying Tanning Extracts. *Bull. Soc. Ind.* through *J. S. C. I.*, XXXI, 400. The natural impurities in the decoctions and extracts are precipitated by addition of resin soap solution, together with finely divided barium (or lead) sulphate to accelerate the precipitation. This process, due to E. Tagliani, has been used by Lepetit, Dollfus and Gansser on a large scale since 1900. Twenty liters of soap solution (15 kilos of rosin and 15 kilos of caustic soda solution of 20° Bé to 250 liters of water) and 1,700 grams of barium sulphate paste (80 per cent.) are added with stirring to 1,000 liters of chestnut wood decoction (2.5-3.5° Bé) previously cooled to 25-30° C., and the mixture allowed to settle. Precipitation is complete in an hour, the clear liquid is drawn off for concentration, and the deposit pressed in a filter press. The extract thus obtained is of a paler color than those purified with blood, etc. Logwood, quebracho and oak decoctions are similarly treated. Better results still can be obtained by first adding a little lead nitrate solution and then ¼ of the above proportions of soap solution and barium sulphate. The process can be applied to ordinary chestnut extract, and the following quantities are given for 1,000 kilos of extract (28° Bé): 66 kilos of barium sulphate paste, 14 kilos of resin and 14 kilos of sodium hydroxide (20° Bé) with 170 liters of water; followed by 2 kilos of sulphuric acid (66° Bé) mixed with 2 liters of water to restore the original acidity. Precipitation is complete in 24 hours; the clear extract obtained is soluble

Digitized by Google

in water, has a density of 25° Bé and is nearly equal to that obtained by treating the decoction. R. Geigy in reporting on the method states that it is useful for colored tannins such as chestnut, quebracho, etc., though larger quantities of reagents than those given are required for good clarification. The process is not suitable for extracts containing tannins yielding gallic acid. (The last two statements seem to contradict what goes before, since the quantities given are for chestnut, and chestnut extract is said to be especially rich in gallic acid.—Ed.)

Several New Fat Preparations for the Leather Industry. W. Eitner. *Gerber,* 1912 [38], 199-200, 213-214. Before the introduction of drum tannage, liquid fats, particularly old fish oil, etc., were added to the reel vats to prevent foaming. Turpentine, rosin and tar oils were also added in rapid tanning processes in agitated liquors, to reduce the action on the grain. This practice was adopted later in drum tanning. Turpentine oil proved unsuitable, since it gave dyeing power to the tanstuff. The general properties which a tanning oil (Gerböl) should possess are high power of emulsification, indifference to the tanstuff and cheapness. Some of these substances are merely strong alkaline or neutral soaps prepared from liquid fat acids (elain) and ammonia; sometimes the fat is in excess. Mixed oils contain an addition of mineral oil; when the soap is dissolved the solution becomes milky, as also in the case of soaps containing excess of fatty acid. Mixed oils containing mineral oil and the soap dissolved in spirit, give clear solutions. Neutral or acid soaps have no unfavorable action upon tannin, but excess of alkali reduces the tanning action and darkens the color. Alkaline oils are, however, much used in quick tanning processes and help dissolve Argentine extract. These tanning oils are only to be used with moving liquors as in reels, rockers and drums and not in layaways and pits, although this is sometimes recommended. A properly made oil is of advantage when giving the grain of sole leather hides a foretannage in sweet liquors before the acid swelling. For chrome tannage, the soap mixtures above referred to are decomposed in the liquors and give inactive chrome soaps. Sulfonated oils are used here, generally from elain.

Another use of oil is as grain oil (Narbenöl) in currying sole leather to prevent hardening of the grain after tannage in strong extracts. Ordinary fat would darken the leather and an emulsion is also needed here, although the miscibility with large amounts of water is not so essential as with the tanning oils. Linseed oil, formerly used, is expensive and soon dries. Neutral elain soap with elain or stearin oil is the best combination for the grain from heavy extracts, while soap with castor and mineral oils can be used when there is less danger of brittle grain. Sulphonated oils are also substituted for the elain soap. A so-called bleaching oil designated as "Kremol" was found to contain 30 per cent. sulfonated fish oil, 70 per cent. mineral oil. The use of these oils originated in the Turkey red (alizarin) dyeing process. Rancid vegetable oils were first used containing oxy-acids which enabled the fiber to fix the dyestuff. A

Digitized by Google

similar effect is produced upon hide by the degras of the chamois leather process. The Turkey red oil, later substituted for the naturally oxidized oil, was produced from castor oil by gradual addition of 20-25 per cent. H_2SO_4. After standing one day, the mixture was washed with salt brine, then water, leaving the acid oil. This neutralized with ammonia or soda gave the neutral product. The writer recommended long ago this red oil which saponifies with soda for preparation of the fat liquor for chrome upper leather; the other fats easily emulsify with it.

Sulphonation has also been tried upon fish and elain oils giving products which have high tanning power. The sulphuric acid is in organic combination and need not be feared. The writer obtained good results in experimental chamoisage with such oils and expects to resume the research. Sulfonated fish, elain or stearin oils are well suited for chrome leather fat liquors and superior to any soap; especially suited is the elain red oil soap.

The preparation of these substances requires technical precision and they are best procured from a reliable maker. W. J. K.

The Fat Content and Specific Gravity of Belting Leather. Dr. Johannes Paessler. *Ledertechn. Rundschau*, 1912, pp. 185-7, 193-5. Definite requirement and specifications of these constants are now being made and especially for this leather. The question arises whether a manufacturer can really control the product. In greasing leather, a definite ratio between the amount of fat applied and that absorbed can be expected and controlled in the drum process or in greasing hot or cold upon the table but not in the dipping process. Ordinarily it is assumed that a single sample of leather represents the entire delivery, which is thoroughly incorrect. The author has found that the same hide varies extraordinarily in fat content according to the location of the test-piece and that various hides subjected to the same treatment contain very diverse amounts of fat. This is due to local differences in structure of the hide, the loose porous parts taking up most fat. Also it may happen with suspended hides that fat may melt and settle by gravitation to the lower parts. The conditions controlling specific gravity are still more complicated and no uniformity can be expected.

The author tabulates the result of determination of fat content and specific gravity in 72 oriented samples from 4 representative hides. The figures vary greatly but some generalizations are drawn. As von Schroeder has already pointed out, a high water content corresponds to low fat and vice versa. The great variation in fat percentage is shown in the summary:

	Left half		Right half		Average entire hide
	lowest	highest	lowest	highest	
Hide No. 1	9.9	20.4	11.8	23.4	16.1
Hide No. 2	15.4	27.2	15.0	26.0	19.3
Hide No. 3	12.8	20.2	12.7	21.1	15.9
Hide No. 4	12.9	19.7	15.4	23.6	17.6

Digitized by Google

In general, the corresponding right and left samples show same fat content. The highest is reached in the belly parts towards the neck; the lowest is found midway between belly and back. The part that best averages the whole is about 10 cm. from the back (on either side) and 10 cm. distant from the rear edge of the hide. If this be analyzed for several hides, a much fairer average will be secured than from a random sample.

The variations in specific gravity are shown in the summary:

	Left half		Right half		Average entire hide
	lowest	highest	lowest	highest	
Hide No. 1	0.925	1.038	0.966	1.035	1.004
Hide No. 2	0.996	1.060	1.002	1.065	1.035
Hide No. 3	0.870	1.026	0.927	1.022	0.980
Hide No. 4	0.925	0.980	0.901	0.995	0.956

The lowest gravities are for the above specified locations giving highest fats. The highest gravities are in strips midway between back and belly. Average values are best shown by the corresponding mid pieces at either end of the hide, therefore the sample recommended for fat determination may also serve for testing the specific gravity. The densities were found greatest in the heavier hides. The specific gravity varies with water content and this should always be specified. W. J. K.

Neutralization of Chrome Leather. Josef Jettmar. *Ledertechn. Rundschau*, 1912, pp. 273-6. This is the most important and difficult operation in the manufacture. Unlike tawed leather, the chrome leather may be washed directly after tannage, but it is better to let the leather rest 12-24 hours, that the tannage may complete itself with less loss of tanning material.

Normally there should be no free acid in the leather since the reduction bath ought contain no excess and the single bath operates with basic salt. If in the latter case too much chrome salt be absorbed, the leather reacts acid for the water splits from the basic salts soluble, acid reacting chrome compounds. Continued washing always removes more or less acid chrome salts, that remaining in the leather becoming more basic and fixed. The washing is sufficient, however, when the leather reacts neutral to litmus; warming and agitation hasten the process. Further, if foreign salts and free acid remain, although a heavy leather may result, it easily forms spew. Free acid decomposes the fat emulsions and smeary chrome soaps coat the leather and dull the grain. Free acid also injures the fiber, giving rough grain and brittle leather; troubles are also caused in dyeing and currying.

Good washing for all these reasons is important. To shorten the process and prevent detannage, neutralizing agents are added to the wash water. It is important not to push this too far. With strong caustic or carbonated alkali, the end product is completely acid free chromium hydrate $Cr_2(OH)_6$. Even if not completed for all the salt present, it is

Digitized by Google

realized in part and gives a brittle leather. Practically, this is avoided by using milder reagents. Chalk is one of these; the natural European mineral, ground and prepared for use, is quite pure calcium carbonate, costing 6.50 marks per 100 kilo. With the basic chrome salt it gives CO_2 and insoluble gypsum. Its use was soon given up, since the chalk could not penetrate the leather and the action was confined to the acid resulting from a slow diffusion; the gypsum produced was also objectionable.

Borax, $Na_2B_4O_7$, is of alkaline reaction, hydrolyzing readily in dilute solutions. It has the advantage over other neutralizing agents in being without effect when used in excess. The weak boric acid freed in reaction has no effect on the basic chrome salt and goes away in the wash water. The salt is, however, expensive and it is economy to use only the computed amounts instead of following a general recipe.

Water glass, Na_4SiO_4, is cheapest in the liquid form of 50-55° B. It is rapid and goes further than borax, but the silica set free fouls the leather. Sodium sulphide has been recommended but the H_2S generated is objectionable. Sodium bicarbonate has also been unsuccessful; the evolution of large amounts of CO_2 set free on neutralizing, easily injures the fiber.

All these reagents are gradually added to the wash water until neutrality is reached. The endpoint for leather which is to be blocked is easily recognized by adding logwood to the liquor; the red hue changes to bluish when neutrality is reached. Usually the reaction of a section of the leather to litmus is used, although this is a matter of estimation, since "neutralized" leather still shows the red reaction. Small amounts of borax do not act on litmus or even phenolphtalein. Eitner tests neutrality by kneading the leather with dilute sol. of oil soap; free acid is detected by the feel which becomes sticky. Kaushke proposes to treat the leather first with a solution of sod. phosphate, HNa_2PO_4; the liberated phosphoric acid is afterwards neutralized by a weak solution of $HNaCO_3$. One advantage claimed is that any sulphuric acid withdrawn from the basic chrome salt through excessive de-acidification, is replaced by phosphoric acid giving an insoluble chromium phosphate. The process has not found favor.

Stiasny has worked out a method which promises well. A mixture (generally equal parts) of sod. carbonate, cryst., and sal-ammoniac is used. This liberates a certain amount of ammonia, the action of which is modified by the excess of sal-ammoniac present. To every 100 kilos leather 2 k. salt mixture are used, dissolved in sufficient water. After drumming 10-15 min., 2 k. more salt are added and further drummed 15-20 min. If neutralization is not complete, the drumming is continued and eventually another portion of salt added. Large amounts of water are used and the requisite amounts of reagent determined by trial.

Double bath leather can be neutralized directly after the reduction bath, first washing in luke warm water. Single bath leather can be let lie over night; it appears that more chrome is thus fixed. If strong liquors

Digitized by Google

have been used, washing follows direct to avoid spotting. If the leather has been tanned in less basic liquors, it may be washed and neutralized in one bath, the acid chrome salt becoming thereby thoroughly basic and fixed.

The fat liquor may be depended upon for the neutralization of slight amounts of acid remaining in the leather. It would be, however, a mistake to make the fat liquor strongly alkaline for neutralization purposes, for the leather would readily spew and could not be dyed or neatly curried. W. J. K.

Hide Preservation and Glue Leather. W. EITNER. *Gerber* [38], 241-3. In April, 1912, the united German manufacturers issued an appeal to the leather makers to discontinue the use of formaldehyde. The glue leather delivered in the summer months refused to dissolve and gave low yields of inferior quality, all of which was traced back to formaldehyde.

The author proceeds to discuss this from the tanner's standpoint. Formaldehyde undoubtedly changes hide to a considerable degree if sufficiently applied, but this lowers the quality of the leather and it is for the interest of the tanner also to avoid such radical use. He is not affected to the same extent as the glue-boiler, however, since it is the flesh (which furnishes most waste) which is most acted upon by the formaldehyde.

The first use of formaldehyde for hide preservation appears to have been made by the Conservadore Mercantile Company in Buenos Ayres. They treat fresh hides direct from the slaughter with formaldehyde vapor. This effects a beneficial sterilization before the usual salting destroying organisms which the salt would not affect. A preliminary sterilization with formaldehyde also works well for hides which are to be dried. Decay is prevented and insects are kept away during the drying. The process further prevents the transportation of disease germs, particularly from pestilential districts. This sterilization with formaldehyde is best made with vapor in closed rooms using known amounts which can be regulated. It has been shown that thus limited, the formaldehyde does not injure the hide in the slightest. It is also practicable to apply a 2.5 per cent. solution with the brush or to hang the hides for several hours in a 2 per cent. solution. A wet process, however, does not seem suitable.

In the above, formaldehyde has not been used for the preservative proper. If, however, solutions of over 5 per cent. be applied to the hide, the formaldehyde itself becomes a preservative. The hide is altered but is still suitable for certain purposes. The unhairing is rendered difficult but this is overcome by the use of sodium sulphide in the limes. The glue leather from this source is of low value and most of the complaints against formaldehyde might properly be laid to the sulphide liming.

The leather maker cannot profitably direct his business to the produc-

Digitized by Google

tion of a low value by-product like glue leather. The glue boiler can at least fall back upon bone, while the tanner has little choice of raw material. W. J. K.

What Action has Sulphuric Acid in the Extraction of Tanning Materials? JULIUS WLADIKA and EMANUEL KUDLACEK. *Collegium* No. 508, pp. 347-379, and No. 509, pp. 433-60. The researches described in this paper were carried out at the Vienna Research Station. A number of tanning materials were extracted with water and with N/5 sulphuric acid, and the resulting liquors studied. The table gives a summary of the most important results. Percentages are on dry basis.

	Water extract			Acid extract		
	Tannin Per cent.	Non-tan. Per cent.	Sugar Per cent.	Tannin Per cent.	Non-tan. Per cent.	Sugar Per cent.
Fir bark	15.4	11.2	1.4	9.6	26.3	15.8
Oak bark	8.2	5.6	0.9	3.7	20.1	10.4
Valonia	32.5	11.7	2.4	32.8	14.7	4.0
Oak wood	9.4	3.9	0.5	8.7	14.9	3.9
Chestnut wood ..	9.7	3.9	1.0	8.3	13.6	3.7
Myrobalans	31.2	12.3	4.7	25.2	15.0	3.5
Sumac	30.1	16.3	3.0	25.1	19.0	3.2

L. B.

Testing of Tanning Extracts with Animalized Cotton. DR. A. GANSSER. *Collegium*, 509, 479-82. Dr. Gansser's animalized cotton is prepared by selecting cotton goods 1 mm. thick with no dressing, cutting it into strips 11 cm. wide and 20 m. long, passing the strips through a 1 per cent. water solution of formaldehyde, wringing them between rubber rolls, passing them 4 times through a 10 per cent. solution of hide gelatin at 600° C., then through the rubber rolls with very slight pressure to distribute the gelatine, and drying by stretching in a horizontal position over wooden rods in an airy room at ordinary temperature. Apparatus for this process is described and illustrated, made of copper and aluminum bronze by the Swiss Metallurgical Society of Basel. Before use the material is soaked ½ hour in water at 15° C. A liquor of 6° Bé at 20° C. is recommended for the tannage. After standing a few minutes, the vessel is put on the rotating shaker for 7 hours. A light rinse is now followed by passing the tanned pieces through rubber rolls with light pressure, or pressing between filter paper. Then dry out of sunlight at ordinary temperature. Traces of copper in an extract give a yellow tone to the test pieces. L. B.

Digitized by Google

Journal of the

American Leather Chemists Association

Vol. VII DECEMBER, 1912 No. 12

W. K. ALSOP . . . . . Editor and Manager
LLOYD BALDERSTON . . . . . Associate Editor

Correspondence pertaining to the Editorial Department should be addressed to the Editor at Ridgway, Pa.

Published Monthly by the American Leather Chemists Association.

Subscription—Members, $5.00 annually; Non-members, $7.00 annually.

Checks for Subscriptions and Advertisements should be addressed to the American Leather Chemists Association.

All Business Communications should be addressed to the Chemical Publishing Company, Easton, Pa.

Entered as Second-class Matter at the Post Office, at Easton, Pa.

Copyright, 1912, by the American Leather Chemists Association.

The American Leather Chemists Association

G. A. KERR, W. H. TEAS, H. C. REED, J. H. YOCUM, F. H. SMALL, H. T. WILSON, J. H. RUSSELL, ... Past Presidents

OFFICERS, 1910-'11

PRESIDENT—F. P. VEITCH, Leather Laboratory, Dept. of Agriculture, Washington, D. C.

VICE-PRESIDENT—R. W. GRIFFITH, 644 Greenwich St., New York, N.Y.

SECRETARY-TREASURER—H. C. REED, Tanning Research Laboratory, 227 Fulton Street, New York, N. Y.

COUNCIL—F. H. SMALL, Worcester, Mass.

C. R. OBERFELL, Harrisonburg, Va.

W. H. TEAS, Marion, Va.

A. W. HOPPENSTEDT, Perry and Mississippi Streets, Buffalo, N. Y

ELECTIONS.

ACTIVE

Walter G. Sprinkel, North Wilkesboro, North Carolina.

ASSOCIATE.

Ogden W. Tunison, South Orange, New Jersey.

CHANGES OF ADDRESS.

George T. Ormerod, Jr., to Briarmead, Whitegates, Middleton, England.
J. S. Robeson to Pennington, New Jersey.
H. T. Wilson, to Canton, North Carolina.
George W. Priest, to 72 Beach St., East Orange, N. J.
R. W. Griffith to 644 Greenwich St., New York, N. Y.

Digitized by Google

NINTH ANNUAL MEETING.

The Ninth Annual Meeting of the American Leather Chemists Association will be held at Washington, D. C., December 5, 6 and 7, 1912. The committee having in charge the arrangements for the meeting has selected the Hotel Raleigh, Pennsylvania Avenue and Twelfth Street, as the place of meeting. A suitable room has been reserved for the meetings, and members who desire to retain rooms at the hotel are requested to apply directly to the management. The following is the schedule of prices:

	Per day
Single rooms without bath	$2.00 and up
Single rooms with bath	3 00 and up
Double rooms without bath	3.00 and up
Double rooms with bath	4.00 and up

PROGRAM.

THURSDAY MORNING, DECEMBER 5, 1912.

Opening Remarks by the President.
Report of the Secretary-Treasurer.
Committee Reports.

THURSDAY AFTERNOON, DECEMBER 5, 1912.

Address, "The Geographic Distribution of Tannin Plants," Dr. W. W. Stockberger, of the Bureau of Plant Industry.
Address, "How Long Should Chestnut-Oak Bark be Stored before Leaching," C. C. Smoot, III.
Address, "Comparative Extract Analysis," C. R. Delaney.

FRIDAY MORNING, DECEMBER 6, 1912.

Committee Reports.
Address, "The Disinfection of Hides," F. W. Tilley, of the Bureau of Animal Industry.

FRIDAY AFTERNOON, DECEMBER 6, 1912.

Address, "Notes on Discussion," Frank M. Loveland.
Address, "The Electrometric Method for Measuring Acidity," Dr. Lloyd Balderston.
(Members who wish to examine the electrometric apparatus and see it work may have the opportunity to do so on Friday evening.)

SATURDAY MORNING, DECEMBER 7, 1912.

Address, "The Identification of Tanned Skins," C. F. Sammet.
Address, (Subject to be announced later), E. J. Haley.
Election of Officers.
General Business.

A paper is expected from Dr. Edmund Stiasny.

Digitized by Google

LEATHER ANALYSIS—A. L. C. A., 1912.

Report on Determination of Sugars in Leather.

By F. P. Veitch and J. S. Rogers.

The Clarification of Leather Extracts for the Determination of Sugar.

The use of basic lead acetate as a clearing agent in the determination of reducing sugars in sugar house products gives low results. This has been shown by many investigations already completed.[1]

Basic lead acetate has been used for clarifying leather extrats for sugar determinations for several years. A. W. Hoppenstedt (1908)[2] in his work for the A. L. C. A. on leather analysis used basic lead acetate. The percentage of glucose found by those co-operating in this work was 1.3 per cent. less than the amount of the glucose actually added to the leather. Hoppenstedt suggests that the low results may be due to fermentation taking place in the leather and thus destroying some of the glucose.

In 1909 Veitch[3] suggested the use of normal lead acetate as a clearing agent in leather analysis, and obtained results closely agreeing with the theoretical. A comparison of normal lead

[1] Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, 1905, **23**, 285-91.
J. B. Mintz, *Bull. Assocn. Chim. Sucr. Dist.*, 1909, **27**, 393.
H. Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, 1909, **27**, 757.
H. Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, **27**, 856.
H. Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, **27**, 861.
H. Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, **27**, 945.
H. Pellet, *Bull. Assocn. Chim. Sucr. Dist.*, **27**, 1070.
J. Mintz, *Centr. Zuckerind.*, **16**, 259.
H. Pellet, *Deut. Zuckerind.*, **35**, 707.
O. Schiefeld, *Z. Ver. Zuckerind., II*, **58**, 947.
C. A. Browne & A. H. Bryan, *Z. Ver. Zuckerind.*, **59**, 922.
Watts, Tempany, *J. Soc. Chem. Ind.*, **27**, 53-58.
L. Eynon, *J. Soc. Chem. Ind.*, **28**, 729.
H. C. P. Geerlings, *Int. Sug. Journ.*, **10**, 432-435.
A. H. Bryan, *Int. Sug. Journ.*, **10**, 602.
H. C. P. Geerlings, *Int. Sug. Journ.*, **11**, 276.
Browne, Halligan, *U. S. Dept. Agri. Bu. Chem. Bull.*, **116**, 68-76.
A. H. Bryan, H. P. Agee, *U. S. Dept. Agri. Bu. Chem. Bull.*, **132**, 175-184.

[2] *J. A. L. C. A.*, v. 3, 255, 1908, Hoppenstedt.

[3] *J. A. L. C. A.*, v. 4, 272, 1909.

Digitized by Google

acetate and basic lead acetate, using the official sample and other adulterated laboratory samples, gave with basic lead acetate results about 2 per cent. lower than with the normal. He concluded that this was due to removal of glucose by the basic lead acetate. In 1911[4] the committee on leather analysis continued using normal and basic lead acetate and they confirmed the results of 1909; that the normal lead acetate gives practically theoretical results while the basic acetate always gives results about 1 per cent. lower than the sugar actually added.

J. G. Parker and J. R. Blockey,[5] using the normal and basic acetates, conclude that the difference in the results is due to the fact that gallic acid (which reduces Fehling's solution) is not completely pptd. by lead acetate in the presence of free acetic acid, and from data on a solution containing tannin, gallic acid and acetic acid, and from the work of Stiasny and Wilkinson,[6] which shows that catechol tannins are soluble in an excess of acetic acid, they conclude that the basic lead acetate gave the more reliable results.

In summing up the literature on the determination of sugar in leather we see that low results have always been obtained with basic lead acetate and that results closely approximating the sugars added to leathers have uniformly been secured by using normal lead acetate as a clarifying agent.

In the work planned for this year an endeavor has been made to eliminate all known sources of error. The dextrose has been added directly to the leather extract with toluol as a preservative to prevent fermentation. ZnO was used in part of the clarifications to neutralize any acetic acid originally present in the leather extract and that liberated by the precipitation of the tannin by the normal lead acetate. Titrations of portions of the filtrates were made to show the total acidity.

Two samples of leather were sent out: (1) An oak tanned sole leather and (2) a hemlock tanned sole leather, both free from added glucose and epsom salts. The directions for the work were as follows:

[4] *J. A. L. C. A.*, v. 6, 565, 1911.
[5] *J. A. L. C. A.*, v. 7, 258, 1912.
[6] *J. A. L. C. A.*, 1911. v. 6, 479. *Collegium*, 1911, 318.

Digitized by Google

Directions for Leather Work—A. L. C. A., 1912.

SOLUTIONS:

Copper Sulphate.

Dissolve 34.639 g. of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos. Prepare 1½ liters.

Alkaline Tartrate Solution.

Dissolve 173 g. of Rochelle salt and 50 g. NaOH in water and dilute to 500 cc. Allow to stand two days and filter through asbestos. Prepare 1½ liters.

Normal Lead Acetate Solution.

Prepare 800 cc. of a saturated solution by placing all of the normal lead acetate sent in a flask, adding 800 cc. H_2O and mixing frequently for a few hours.

Basic Lead Acetate Solution.

Prepare one liter of saturated solution by placing all of the basic lead acetate sent in a flask, adding 1 liter of H_2O and mixing frequently for a few hours.

Make water extractions as directed below by the Bu. of Chem. method *or* by the A. L. C. A. method. Avoid as far as possible any change in the moisture condition of the sample during weighing.

EXTRACTION OF SAMPLES:

A. Place loosely in extraction thimbles three portions (15 g. each) of the sample as received. Extract for 6 hours, with petroleum ether distilling below 80° C. Spread the leather residue on a large watch glass and allow the ether to evaporate. Moisten thoroughly with distilled water. Transfer leather and water to a Soxhlet extractor and place cotton above and below the leather in the extractor to prevent it from being carried over at the time of the syphoning. The cylinder of the extractor shall be surrounded by water-bath kept at 50° C. At the beginning of the extraction pour 200 cc. of distilled water (including that used in moistening the leather) into the Soxhlet and allow it to syphon into the flask below, then begin the boiling. At

Digitized by Google

the end of the first hour remove the flame and transfer the extract to a one-liter graduated flask, add 175 cc. distilled water to the Soxhlet, and continue the extraction for two hours. Remove the extract, add 175 cc. of water and continue the extraction for three hours and remove the extract. Make two more extractions adding 175 cc. of water as before, and continuing the extraction for 4 hours. This gives 14 hours extraction and extracts that do not exceed one liter in volume. Make the extracts up to one liter at room temperature.

B. Extract 2 portions of leather (30 g. each) with petroleum ether as directed above. Then make water extraction by regular A. L. C. A. method.

After diluting the extracts to volume place those obtained from the oak leather in one large container and those from the hemlock leather in another and mix each thoroughly.

The above method of preparing the extracts will give one extract of an oak tanned leather and one extract of a hemlock tanned leather. The volume of each of these extracts will be 3 liters (if prepared by Bu. Chem. method) or 4 liters if prepared by the A. L. C. A. method. Add 4 drops of toluol to each extract, mix and stopper tightly. Weigh into each of two dry 2-liter flasks 1.6826 g. of c. p. dextrose. (Use that sent with sample.) Measure into the first flask exactly 1,400 cc. of the oak extract and into the second flask 1,400 cc. of the hemlock leather extract and mix each thoroughly.

Determine sugar both on the original extracts and on those to which the sugar has been added, by the three methods described below. Make duplicate clarifications and run duplicate sugar determinations on each solution after hydrolysis and neutralization.

Glucose.

(1) Place 200 cc. of the leather extract in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, mix thoroughly (5-10 min.) and filter. The funnels and beakers must be kept covered to prevent evaporation. Add to the filtrate an excess of solid potassium oxalate, mix frequently for 15 min. and filter, returning the filtrate until clear. Pipette 150 cc. of

Digitized by Google

this filtrate[7] into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hrs. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly 4 min.* and boil for 2 min.[8] Filter immediately without diluting, through asbestos, wash thoroughly with hot water, then with alcohol, and finally with ether; dry for half an hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull. 107, Rev. Bu. Chem., p. 243) and report in percentage on leather as received, *or report as* Cu_2O giving weight of Cu_2O obtained in the determination.

(2) Determine sugar in the same manner as in (1) except that instead of using 25 cc. of saturated normal lead acetate, use 25 cc. of saturated basic lead acetate.

(3) Place 200 cc. of leather extract in a 500 cc. flask, add 1.5 g. ZnO, mix thoroughly, add 25 cc. of saturated solution of normal lead acetate, mix thoroughly, proceed as in (1).

Report all results on tabular form which accompanies directions.

The results given by those co-operating are shown in the following tables:

[7] After you have clarified the extract, removed the lead by potassium oxalate, and pipetted the 150 cc. required for sugar determination titrate 25 cc. of the remaining filtrate with $N/_{10}$ hydrate using phenol phthalein, and report the results in cc. $N/_{10}$ hydrate required per 25 cc. of filtrate. It may be necessary to combine the filtrates from the duplicate clarifications in order to obtain a 25 cc. solution.

[8] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. of copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H^2O in a 400 cc. beaker to 100° C. in exactly four minutes.

Digitized by Google

TABLE I.

PERCENTAGES OF SUGAR FOUND BY DIFFERENT METHODS OF CLARIFICATION.

		Oak Leather Extract										Hemlock Leather Extract									
		Original Extract					Orig. Ext. + 1.2g. Dextrose per liter					Original Extract					Orig. Ext. + 1.2g. Dextrose per liter				
		1	2	3	4	Aver.	1	2	3	4	Aver.	1	2	3	4	Aver.	1	2	3	4	Aver.
J. M. Seltzer, Kistler Lesh Co., Lock Haven Pa.	A	0.42	0.45	0.44	0.48	0.45	8.68	8.74	8.60	8.79	8.70	1.07	1.14	1.09	1.10	1.10	9.28	8.96	8.95	9.12	9.08
	B	0.32	0.27	0.32	0.29	0.30	6.75	6.81	6.79	6.84	6.80	0.54	0.56	0.52	0.61	0.56	6.68	6.72	6.71	6.75	6.77
	C	0.38	0.40	0.40	0.45	0.41	8.60	8.56	8.52	8.65	8.56	0.77	0.76	0.81	0.80	0.79	8.69	8.80	8.66	8.71	8.72
J. S. Rogers, Bu. of Chemistry, Washington, D.C.	A	0.38	0.48	0.30	0.30	0.365	8.42	8.44	8.54	8.52	8.48	1.02	1.04	0.92	0.98	0.99	8.96	9.06	9.00	8.84	8.965
	B	0.26	0.16	0.12	0.14	0.17	7.38	7.34	7.30	7.20	7.305	0.46	0.42	0.26	0.42	0.39	7.14	7.04	7.16	7.06	7.10
	C	0.28	0.28	0.24	0.26	0.205	8.14	8.14	8.30	8.28	8.215	0.70	0.68	0.46	0.58	0.605	8.46	—	8.52	8.56	8.513
L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.	A	0.87	0.86	0.94	1.01	0.92	8.80	8.72	8.64	8.79	8.74	1.16	1.18	1.05	1.04	1.11	9.03	9.00	9.07	9.04	9.035
	B	0.63	0.50	0.57	0.50	0.55	7.08	7.05	7.03	7.02	7.045	0.48	0.54	0.48	0.48	0.495	7.16	7.10	—	—	7.13
	C	0.58	0.55	0.72	0.78	0.66	8.35	8.42	8.15	8.26	8.295	0.75	0.70	0.70	0.75	0.725	8.32	8.36	8.32	8.32	8.33
R. E. Drake, Weber & Drake, Boston, Mass.	A	0.90	0.80	0.80	0.90	0.85	8.66	8.62	8.78	8.82	8.72	1.52	1.34	1.32	1.40	1.40	9.34	9.38	9.20	9.24	9.28
	B	0.38	0.46	0.38	0.46	0.42	6.68	6.88	6.90	6.99	6.86	0.30	0.50	0.54	0.66	0.50	6.62	6.62	6.88	7.02	6.82
	C	0.60	0.72	0.64	0.74	0.675	8.58	8.48	8.40	8.44	8.48	0.90	0.86	1.06	0.98	0.94	8.84	8.96	9.06	9.02	8.98
C. B. Bacon, Bu. of Chemistry, Washington, D.C.	A	0.62	0.49	0.56	0.44	0.53	8.50	8.52	8.61	8.64	8.56	0.93	0.88	1.06	0.86	0.93	8.82	8.84	9.08	9.00	8.93
	B	0.41	0.36	0.26	0.28	0.33	7.19	7.19	7.24	7.30	7.23	0.20	0.28	0.49	0.41	0.34	7.21	7.12	7.35	7.22	7.22
	C	0.49	0.41	0.21	0.20	0.33	8.32	8.41	8.34	8.36	8.35	0.54	0.60	0.72	0.56	0.60	8.26	8.20	8.34	8.41	8.30
L. M. Richeson, C. R. Oberfell. England-Walton Lab., Harrisonburg, Va.	A	0.57	0.57	0.57	0.56	0.57	8.07	8.08	7.93	8.04	8.03	0.74	0.70	0.69	0.67	0.70	8.85	8.74	8.76	8.64	8.75
	B	0.37	0.29	0.43	0.37	0.36	6.18	6.28	6.41	6.16	6.27	0.33	0.31	0.35	0.34	0.33	6.57	6.38	6.33	6.43	6.43
	C	0.36	0.31	0.43	0.31	0.36	8.26	8.37	8.22	8.26	8.28	0.69	0.59	0.60	0.60	0.62	8.20	8.30	8.19	8.22	8.23

A, Results obtained with normal lead acetate alone. B, Results obtained with basic lead acetate alone.
C, Results obtained with normal acetate + 1.5g. ZnO.

Digitized by Google

TABLE II.—INDIVIDUAL AVERAGES.

Analysts		Oak leather Ex. cleared with—			Hemlock leather Ex. cleared with—		
		Normal	Basic	Normal + ZnO	Normal	Basic	Normal + ZnO
J. M. Seltzer, Kistler, Lesh & Co., Lock Haven, Pa.	Per cent. Blank on leather	0.45	0.30	0.41	1.10	0.56	0.79
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.70	6.80	8.56	9.08	6.77	8.72
	+ or — error	+0.25	—1.50	+0.15	—0.02	—1.79	—0.07
J. S. Rogers, Bu. Chemistry, Washington, D. C.	Per cent. Blank on leather	0.36	0.17	0.26	0.99	0.39	0.60
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.48	7.30	8.21	8.96	7.10	8.51
	+ or — error	+0.12	0.87	—0.05	—0.03	—1.29	—0.09
L. A. Cuthbert, Elk Tanning Co., Ridgway, Pa.	Per cent. Blank on leather	0.92	0.55	0.66	1.11	0.50	0.73
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.74	7.05	8.30	9.04	7.13	8.33
	+ or — error	—0.18	—1.50	—0.36	—0.07	—1.37	—0.40
R. E. Drake, Weber & Drake Boston, Mass.	Per cent. Blank on leather	0.85	0.42	0.68	1.40	0.50	0.94
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.72	6.86	8.48	9.28	6.82	8.98
	+ or — error	—0.13	—1.46	—0.20	—0.12	—1.62	+0.04
C. B. Bacon, Bu. Chemistry, Washington, D. C.	Per cent. Blank on leather	0.53	0.33	0.33	0.93	0.34	0.60
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.56	7.23	8.35	8.93	7.22	8.30
	+ or — error	+0.03	—1.10	+0.02	0.00	—1.12	—0.39
L. M. Richeson, C. R. Oberfell, England-Walton, Harrisonburg, Va.	Per cent. Blank on leather	0.57	0.36	0.36	0.70	0.33	0.62
	Per cent. Dextrose added	8.00	8.00	8.00	8.00	8.00	8.00
	Per cent. Sugar found	8.03	6.27	8.28	8.75	6.43	8.23
	+ or — error	—0.54	—2.09	—0.08	+0.05	—1.90	—0.39

Digitized by Google

TABLE III.

GENERAL AVERAGES OF ALL ANALYSTS.

	Oak leather extract with			Hemlock leather ext. with		
	Normal	Basic	Normal + ZnO	Normal	Basic	Normal + ZnO
Per cent. blank on leather.	0.61	0.35	0.45	1.09	0.44	0.71
Per cent. sugar added.....	8.00	8.00	8.00	8.00	8.00	8.00
Per cent. sugar found.....	8.54	6.92	8.36	9.00	6.91	8.51
+ or — error.....	—0.07	—1.43	—0.09	—0.09	—1.53	—0.20

TABLE IV.

ACIDITY OF FILTRATES AFTER CLARIFICATION.

AS ACETIC ACID.

	Oak leather extract					
	Original extract			Original extract + sugar		
Analysts	Normal Per cent.	Basic Per cent.	Normal + ZnO Per cent.	Normal Per cent.	Basic Per cent.	Normal + ZnO Per cent.
J. M. Seltzer	0.08	alk.	alk.	0.08	alk.	alk.
J. S. Rogers.....	0.09	alk.	alk.	0.09	alk.	alk.
C. B. Bacon	0.09	alk.	alk.	0.09	alk.	alk.
Richeson & Oberfell ...	0.06	0.005	0.003	0.06	0.004	0.005
	Hemlock leather extract					
J. M. Seltzer	0.06	neut.	neut.	0.06	alk.	alk.
J. S. Rogers.....	0.07	alk.	alk.	0.07	alk.	alk.
C. B. Bacon	0.07	alk.	alk.	0.07	alk.	alk.
Richeson & Oberfell ...	0.05	alk.	alk.	0.05	alk.	0.005

COMMENTS OF ANALYSTS.

J. M. SELTZER:

"The results indicate that normal lead acetate is the proper reagent to use for the precipitation of the tannins in the determination of sugar, and also show that basic lead acetate gives results which are very much too low.

"The method using normal lead acetate and zinc oxide seems to be an excellent one since the acids are neutralized by the zinc oxide, thereby preventing the solution of any lead salts of tannin which might take place in an acid solution.

"The solutions from the oak leather, after hydrolysis and neutralization with normal lead acetate, were slightly colored; with basic lead acetate, colorless; with normal lead acetate + zinc oxide, slightly colored.

"The solutions from the hemlock leather were: with normal lead acetate, highly colored; with basic lead acetate, colorless; with normal lead acetate + zinc oxide, slightly colored."

Digitized by Google

L. A. CUTHBERT:

"Of the three methods submitted I prefer the normal lead acetate method and found that it gave me the best results in every case. This method gave the highest results and in the samples to which dextrose had been added the percentages came very close to what might have been expected. Basic lead acetate gave the lowest results and did not seem to give the correct amount of dextrose actually present. The normal lead acetate and zinc oxide method seemed to have an average, approximately, between the first two methods and presented no more difficulty except in the extra time employed. Besides having a little difficulty at first in determining when sufficient potassium oxalate had been added and getting a few turbid filtrates when using basic lead acetate, I had no other trouble."

CHAS. R. OBERFELL and L. M. RICHESON:

"I have very little to offer in the way of comments on the work, except that I prefer to work with anhydrous sodium carbonate rather than potassium oxalate. Sodium carbonate seems to me to be a safer and surer agent to use for the removal of excess Pb."

J. S. ROGERS:

"The addition of dextrose directly to the leather extract precludes (1) incomplete extraction of sugar from the leather, and (2) fermentation of the sugar while in the leather. The addition of the preservative to the extract prevents fermentation of the added sugar. A practically colorless filtrate can be obtained from an extract of a hemlock leather, if filtration be made immediately after addition of the acetate and the lead be removed from this filtrate at once by precipitation with potassium oxalate. Some color will develop in this filtrate; very slowly if not exposed to the air—more readily if exposed. ZnO in combination with normal lead acetate neutralizes any acetic acid originally present in the leather extract and also the acetic acid liberated by the precipitation of the tannin. It yields a filtrate which is neutral or slightly alkaline. Each of the three methods of clarification gave a blank on leathers to which no sugar had been

Digitized by Google

added. Although this blank is always higher on the hemlock leather than on the oak, this is not due to a higher acidity of the hemlock filtrate (see acidity, table IV) because the acidity shown by this filtrate is less than that shown by the filtrate from the oak. The blanks obtained when the basic acetate and the normal acetate plus ZnO were used were not due to solubility of the lead precipitate in acetic acid because these filtrates were alkaline."

The results which have been obtained this year are exceptionally good. The procedure adopted has eliminated the possibility of errors due to fermentation and incomplete extraction. The results show there is not enough acetic acid produced in the reaction between normal lead acetate and tannins to materially affect the results by the normal acetate method. It will be remembered that at our last annual meeting the point was made that the solubility, especially of the catechol tannins, in acetic acid would lead to high results by this method. The results, where normal acetate and zinc oxid were used, furnished conclusive evidence as to the accuracy of the normal acetate method and the inaccuracy of the basic lead acetate method. It is possible that further experience with the zinc oxide, especially in the presence of much larger quantities of free acids, will indicate that it is better to use zinc oxide in all cases with the normal acetate. Where zinc oxide is used there is a slight tendency for the copper oxide to adhere to the sides and bottom of the beaker and one must of course be careful to remove this entirely. The results obtained this year are so striking that comment is almost superfluous. We may be pardoned, perhaps, for directing special attention to the fact that the results with basic lead acetate, on the copper reducing materials in the extracts, plus the added dextrose, are in all cases lower than the dextrose actually added, thus finally disposing of a procedure for the determination of sugar in leather based on the use of basic lead acetate. Parker and Blockley, in the article referred to above (*loc. cit.*), have as a matter of fact simply confirmed the results of this Association on the determination of sugars in leather, but without evidence against the normal acetate on leather extracts. In fact, in the face of their own data and the data of this Association, they argue against its use.

Digitized by Google

Conclusions.

1. Basic lead acetate removes or destroys sugar actually present in the leather extract.

2. The difference in results obtained by use of the normal and basic lead acetates on an extract from a leather loaded with glucose is not explained by the assumption that more tannic acid, gallic, acid, etc., have remained unprecipitated in the clarification by the normal than by the basic lead acetate.

3. The acidity of a leather extract due to acetic acid, plus the acetic acid liberated in clarification with normal lead acetate, is very small, seldom if ever exceeding 0.15 per cent.

4. When normal lead acetate is used as a clearing agent for leather extracts, concordant results are obtained which show more nearly the actual sugar content of the leather than do the results obtained when basic lead acetate is used.

Recommendations.

Your committee recommends the following as the official method for the determination of glucose in leathers.

Solutions:

Copper Sulphate.

Dissolve 34.639 g. of $CuSO_4.5H_2O$ in distilled water and dilute to 500 cc. Filter through asbestos.

Alkaline Tartrate Solution.

Dissolve 173 g. of Rochelle salt and 50 g. NaOH in water and dilute to 500 cc. Allow to stand two days and filter through asbestos.

Normal Lead Acetate Solution.

Prepare a saturated solution of normal lead acetate.

Determination of Glucose.[9]

Place 200 cc. of leather extract of analytical strength in a ½-liter flask, add 25 cc. of a saturated solution of normal lead acetate, shake frequently (5-10 min.), and filter. (The funnels

[9] The rate of heating of the Bunsen burner used should be regulated before sugar determinations are started. This is best done by adjusting the burner so as to bring 25 cc. copper soln. + 25 cc. alk. tartrate soln. + 50 cc. H_2O in a 400 cc. beaker to 100° C. in exactly four minutes.

Digitized by Google

and beakers must be kept covered to prevent evaporation.) Add to the filtrate an excess of solid potassium oxalate. Mix frequently for 15 min. and filter, returning the filtrate until clear. Pipette 150 cc. of this filtrate into a 600 cc. Erlenmeyer flask, add 5 cc. of concentrated HCl and boil under a reflux condenser for 2 hrs. Cool, neutralize (place a small piece of litmus paper in the flask) with anhydrous sodium carbonate, transfer to a 200 cc. graduated flask and make to volume. Filter through a double filter. (The filtrate must be clear.) Determine the dextrose in the solution immediately.

Place 25 cc. of the copper solution and 25 cc. of the alkaline tartrate solution in a 400 cc. beaker. Add 50 cc. of the clarified and neutralized solution above mentioned and heat to boiling in *exactly 4 min.* and boil for 2 min. Filter immediately without diluting, *through asbestos,*[10] wash thoroughly with hot water, then with alcohol, and finally with ether; dry for half an hour in water oven and weigh as cuprous oxide, determine the amount of dextrose by the use of Munson and Walker's table (Bull 107, Rev. Bu. of Chem., p. 243) and report in percentage on leather.

REPORT OF THE 1912 COMMITTEE ON "OILS AND FATS."

By Charles R. Oberfell, Chairman.

In regard to the sulfonated oils to which the Council wished attention to be directed this year it seems that the desired object of this committee is to find suitable methods whereby the purchaser can be assured that he is receiving what he pays for rather than to prescribe tests to show a particular adaptation of an oil to a certain purpose. The general constitution of sulfonated oils is known and the multitude of uses to which they are put in the manufacture of all classes of leather makes it entirely unpractical to prescribe tests to determine the fitness of an oil for a particular use. With this in mind it seems that a proximate analysis is what is desired. Naturally the ultimate

[10] The finely divided, long-fibered asbestos to be used in the glucose should be digested with HNO_3, washed, then digested with NaOH and washed. When gooch-filters are prepared they should be washed with boiling Fehling's solution, then with HNO_3. The mats thus prepared can be used for a long time.

Digitized by Google

constitution is of importance especially to the chemist but its practical bearing is nil.

The identification of the fatty oil from which the product was made is of practical import, but will necessarily have to be deferred due to the difficulty of the problem. With no tests for the positive identification of oils in admixture the problem is complicated in an oil which has been treated with concentrated sulfuric acid and subsequently with a strong base. It seems, therefore, that we should direct our energies first to the selection or invention of methods so that it can be definitely said how much fatty material a sample contains.

Various methods have been suggested for the estimation of the fatty acids, both neutral and combined with sulfate radical, but what is of more importance is the amount of original oil (glyceride) present and whether adulterated with mineral oils. Mineral oil in such an instance is an adulteration although its presence will not make the oil unsuitable for most purposes. If the tanner wants the sulfonated oil to contain mineral he can add it, or which amounts to the same thing a sulfonated oil containing mineral oil should sell for proportionately less.

Our proximate analysis then will be as follows with a few side qualitative tests for neutrality and base used:

Water and Volatile Matter.
Ash.
Non-Saponifiable.
Fatty Oils.

The following methods were sent to the committee together with two samples, the second sample being the same as the first with addition of about 20 per cent. of mineral oil. These two samples thus arranged give a suitable opportunity for judging the merits of the method for the removal of the non-saponifiable, one of the most difficult with which we have to deal.

Sulfonated or Sulfated Oils.

Proximate Analysis.

Water and Volatile Matter.

Method I.—1. Weigh about 10.0 grams of sample into a weighed dish with small glass rod (same size and shape used in

Digitized by Google

tannin determination) and heat for 16 hours in oven at 95-100° C. Stir occasionally. Cool and weigh.

1a. Replace dish from 1, dry 2 hours. Cool and weigh.

1b. Replace dish from 1a, dry 2 hours. Cool and weigh.

Method II.—1. Weigh about 10.0 grams into a weighed dish with small glass rod (same as in Method I) containing about 50 grams previously acid washed and ignited sea sand. Mix oil and sand thoroughly and dry as in Method I, 1, 1a and 1b.

Crucible Method.—Weigh about 1.0 gram into a crucible (about 25 cc. capacity) and heat with free small flame until all water has been expelled gently. The end is indicated by tiny puffs of smoke, which are easy to observe. Cool and weigh.

Ash.

Method I.—Weigh into a dish about 10.0 grams of sample and heat in sand bath until the oil smokes and begins to char, then continue heating over flame and finally ignite until all carbon is consumed. Cool and weigh.

Crucible Method.—Ignite residue remaining in crucible from moisture determination by crucible method. Cool and weigh.

Non-Saponifiable.

Weigh about 10.0 grams into a 500 or 600 cc. flask. Add 25 cc. alcohol-KOH solution (10.0 gms. KOH in 100 cc. alcohol) and 100 cc. petrolic ether, B.P. 40-75° C. Boil, use condenser having sufficient surface to prevent loss of much of the benzin, for 60 minutes. Add 100 cc. of water. Cool. Transfer to 500 cc. pear shaped separatory funnel. Draw off soap solution as soon as separated and wash ether layer with 3 to 5 portions of water of at least 100 cc. Shake out soap solution 3 times with 50 cc. petrolic ether, combining ether extracts and reserving them for subsequent washing with water in funnel to make positive elimination of all soap. After final washing the ether solution is drawn off, heated gently to aid separation of particles of water and finally evaporated in a tared beaker or crystallizing dish. Cool and weigh. Reweigh for approximately constant weight. Alcohol may be used to break emulsions and it is most effective when the emulsion has been drawn into the narrow portion of the funnel.

Digitized by Google

Total Fatty Oil. (Original Glyceride).

Obtained by difference between 100 and the sum of the combined percentages of water and volatile matter, ash and non-saponifiable.

Ammonia as Base or Finisher. (Qualitative).

Add excess NaOH and heat. Test fumes with moist litmus paper.

Reaction.

Dissolve some of the oil in water and test solution with phenolphthalein and litmus.

Comments—Water and Volatile Matter.—The results indicate that method II using sand and heating for 16 hours is as efficient as method I, drying for 20 hours. There is apparently little difference between method II and the crucible method and satisfactory duplicates can be obtained with little practice. It is to be preferred on account of ease and rapidity of manipulation.

Ash.—Either method for ash is satisfactory.

Non-saponifiable.—Much better results were obtained than expected by the chairman. Mr. Cuthbert objects to the method proposed because it consumes too much ether, but this can hardly be of any consideration in view of the absolute necessity and difficulty of extracting all the non-saponifiable from the soap. Another member had difficulty with the digestion due to bumping and criticized the addition of the ether in the boiling flask. This is not an essential point, but strange, it was added for the purpose of preventing such bumping and has proved very efficient in this respect.

Ammonia.—Any ammonia present is expelled largely in the water and volatile matter determination and is calculated as volatile matter. It is again expelled in the ash determination so that it exerts no appreciable error on the total fatty material content arrived at by difference.

Reaction.—Some analysts make an estimation of any free sulfuric acid, but your chairman did not have time this year to go into this problem and refers it to any subsequent committee along with the problem of identifying the source of the fatty material.

Digitized by Google

SULPHONATED OILS.

Sample "A."

	Water and volatile matter							Ash				
	Method I			Method II			Crucible method	Crucible method	Dish method	Non-saponifiable	Ammonia	Reaction
	1	1a	1b	1	1a	1b						
W. G. Sprinkel and C. C. Smoot III..	—	—	25.31	—	—	25.15	24.79	5.71	5.71	1.71	none	acid
C. Eachus.....	25.39	25.37	25.37	24.75	24.90	24.92	26.17*	—	5.65	4.44	"	"
L. M. Richeson.....	23.85	24.59	25.10	24.94	25.01	25.09	24.58	5.63	5.72	2.78	"	"
C. R. Oberfell.....	24.00	24.71	25.17	24.73	24.76	24.85	24.63	5.84	5.80	2.45	"	"
L. A. Cuthbert.....	24.74	25.10	25.24	24.67	24.77	24.69	24.76	5.58	5.66	3.10	"	"
F. O. Sprague	24.59	25.07	25.21	24.87	24.88	24.94	23.28	5.87	5.60	1.01	"	"
J. S. Rogers	25.45	25.58	25.66	25.20	25.21	25.27	26.17	5.80	5.69	2.81	trace	"
Average	24.67	25.07	25.29	24.86	24.92	24.99	24.91	5.72	5.69	2.61		

Sample "B."

W. G. Sprinkel and C. C. Smoot III..	—	—	24.06	—	—	24.00	23.49	5.03	5.09	20.14	none	acid
C. Eachus.....	23.52	24.10	24.36	23.85	24.16	24.20	25.30*	—	6.04†	22.90	"	"
L. M. Richeson.....	19.15	21.52	22.62	23.93	24.02	24.05	23.44	5.00	5.10	20.77	"	"
C. R. Oberfell.....	21.58	23.37	24.00	23.84	23.86	23.94	23.48	4.98	5.01	20.93	"	"
L. A. Cuthbert.....	23.20	23.82	24.07	23.77	23.74	23.73	23.65	5.04	5.04	21.56	trace	"
F. O. Sprague	22.59	23.62	23.86	23.80	23.87	23.90	23.43	5.02	5.02	23.14	none	"
J. S. Rogers	23.68	24.15	24.35	24.45	24.53	24.68	23.89	5.05	5.03	21.02	"	"
Average.....	22.29	23.43	23.90	23.94	24.03	24.07	23.58	5.02	5.06	21.49	"	"

* Pt. dish used in place of crucible. † Not in average.

Digitized by Google

Mineral Oils.

The samples sent to the committee were selected to cover as wide a range of variation as possible. It is pretty definite that the percentage evaporation can be changed by varying the temperature at which the determination is made, it is also definite, as proved by last year's work that with a well refined oil or one with a low volatile content there is only a small difference between a temperature used of 65° and 100° C. In view of the above it seemed fair to select a temperature at which well refined oils will not be placed at a disadvantage but at which an oil high in volatile matter can easily be detected at the same time selecting a temperature within easy and constant reach in any laboratory, *i. e.*, 95-100° C. or the usual temperature of any steam or water oven. It is essential to employ some means whereby a uniform surface is exposed during heating. Filter paper has been recommended but its use introduces some difficulty in getting the oil spread on an absolutely dry piece without the absorption of moisture and resultant error therefrom. Sand was tried this year as a substitute for paper and a 2 inch dish, crystallizing pattern, containing 10.0 grams of sand appears to offer the best surface. If under the conditions prescribed uniform results can be obtained they should be adopted because other procedures can be drawn which no doubt would give variant results, but this year's method is the result of several years of observation and is absolutely fair to every oil.

The work of the committee however, demonstrated that concordant results can not be obtained and in view of similar results last year it seems that the use of sand offers only a slight advantage over a plain dish. From the work of this committee I am very much in doubt as to the probability of developing a satisfactory evaporation method.

Gravity.—The results were so uniform as to recommend the adoption of the method proposed.

Viscosity.—The chairman secured uniform viscosity pipettes in the hope that by its use concordant results would be obtained, but the data returned utterly destroyed this hope, and I feel that the pipette will have to be abandoned. Recently Mr. Balderston has written me that he is obtaining promising results from the

Digitized by Google

use of an instrument devised by Gurney and measuring absolute viscosity and this may be worthy of trial by this committee another year.

Flash Point.—The results returned were very satisfactory with the common appliance used, and this test may have to be used in place of the evaporation determination.

Mineral Leather Oils.

Mineral Oil Tests.

Gravity.

Cool the oil to 15.5° C. and place in a water-bath at this temperature during balancing. Use a Westphal balance and see that it is in standard condition before use.

Evaporation.

1. Weigh about 1.0 gram sample into a weighed crystallizing dish or low beaker 2" (inches) diameter, containing small glass rod and about 10.0 grams previously acid washed and ignited sea sand. Mix oil and sand thoroughly and dry in oven at 95-100° C. for 16 hours. Cool and weigh.

1a. Replace dish from 1, dry 2 hrs. Cool and weigh.

1b. Replace dish from 1a, dry 2 hrs. Cool and weigh.

1c. Replace dish from 1b, dry 2 hrs. Cool and weigh.

Viscosity.

Use pipette supplied. Test same with water at 20° C. and report in seconds in connection with your results. Use stop watch if possible. Bring the oil to 20° C. in a room at 20° if possible. If not report temperature of room with results. Allow the oil to flow and record number of seconds required.

Reaction.

Heat about 15 cc. of oil with 50 cc. distilled water in a test tube. Draw off water and test its reaction with a solution of litmus. With methyl orange or phenolphthalein if litmus is not at hand.

Asphaltic Bases and Tar.

Place 5 cc. of oil in a separatory funnel of about 200 cc. capacity. Add 95 cc. petroleum ether. Shake thoroughly and run into a 100 cc. graduated cylinder. Allow to settle and report volume of precipitate.

Digitized by Google

MINERAL OIL "1."

	Gravity	Evaporation 1 Per cent.	1a Per cent.	1b Per cent.	1c Per cent.	Viscosity	Flash point °C.	Reaction	Tar bases
Sprinkel & Smoot	0.9329	—	—	—	17.16	580.4	177.5	neutral	none
Eachus	0.932	13.80	14.91	15.10	15.21	—	162.0	"	"
Richeson	0.933	9.34	10.21	10.95	11.69	595.8	174.0	"	"
Oberfell	0.9321	7.05	7.55	7.98	8.63	591.8	172.0	"	"
Cuthbert	0.9317	8.74	9.63	10.42	11.29	735.7	170.0	"	"
Sprague	0.9310	11.33	12.67	13.80	—	488.0	178.0	"	"
Rogers	0.9312	17.01	18.51	19.67	20.98	562.0*	183.0	"	"

Sample "2" Mineral Oil.

Sprinket & Smoot	0.8983	—	—	—	3.67	407.5	202.5	"	"
Eachus	0.8982	3.21	3.62	3.84	3.90	—	193.0	"	"
Richeson	0.9000	2.32	2.58	2.79	2.90	378.9	199.0	"	"
Oberfell	0.8989	2.17	2.31	2.53	2.74	384.8	195.0	"	"
Cuthbert	0.8973	2.38	2.65	2.77	2.99	487.1	195.5	"	"
Sprague	0.8980	3.26	3.54	3.99	—	345.5	190.0	"	"
Rogers	0.8973	4.41	4.94	5.23	5.73	400.0*	205.0	"	"

Sample "3" Mineral Oil.

Sprinkel & Smoot	0.8727	—	—	—	1.09	483.5	212.5	"	"
Eachus	0.8723	0.69	0.92	0.97	0.98	—	212.0	"	"
Richeson	0.8750	0.67	0.72	0.78	0.77	449.3	215.0	"	"
Oberfell	0.8733	0.69	0.69	0.82	0.82	445.1	210.0	"	"
Cuthbert	0.8710	0.40	0.47	0.45	0.53	555.7	210.0	"	"
Sprague	0.8710	0.85	0.79	1.07	—	375.8	215.0	"	"
Rogers	0.8710	1.05	1.36	1.33	1.52	466.0*	225.0	"	"

Sample "A" Mineral Oil.

Sprinkel & Smoot	0.8692	—	—	—	5.71	344.1	122.5	"	"
Eachus	0.8692	5.28	5.53	5.66	5.70	—	100.0	"	"
Richeson	0.8690	5.28	5.38	5.45	5.44	312.7	119.0	"	"
Oberfell	0.8680	5.33	5.33	5.49	5.49	319.5	115.0	"	"
Cuthbert	0.8677	5.12	5.21	5.18	5.26	404.3	Under 150.0	"	"
Sprague	0.8690	5.37	5.40	5.46	—	275.8	167.0	"	"
Rogers	0.8675	5.52	5.26	5.78	5.88	345.0*	150.0	"	"

* Room 27.5° C.

Digitized by Google

Flash Test.

Set a procelain crucible 60 mm. top diameter; 25 mm. bottom diameter; and 50 mm. high. (Any open cup of approximately this size will serve) in a sand bath so that the top is below the rim of the bath. Fill cup to within ¼" of top. Adjust thermometer in center of the liquid. Apply heat so that the temperature rises 8° C. per minute and apply test flame first at 150° C. and then at every rise of 2.5°. Use jet flame approximately 8 mm. long and 3 mm. diam. Apply flame by passing slowly and completely across the cup about ½" above the level of the oil and just in front of the thermometer.

THE DETECTION AND ESTIMATION OF TANNING MATERIALS IN ADMIXTURE.

Committee Report, 1912.

By A. W. Hoppenstedt, Chairman.

To the members signifying their desire to co-operate in the work of the committee, the chairman sent the following instructions:—

As the subject of the detection and estimation of tanning materials in admixture is at present one which largely calls for individual research and effort, and not readily applicable to a committee, the chairman is of the opinion that the following work which he requests you to do, will constitute as much as can be accomplished this year.

The work consists in giving the two tests published by the chairman in the March, 1912 number of the JOURNAL, for the detection of Mangrove and Hemlock, a thorough trial, and on as many pure samples of these tanning materials as possible.

1. Test as many samples of pure Mangrove and Hemlock as possible, using the respective tests, and note how the various samples of each agree and also any features that may be of interest. Report to me your observations and also the number and origin of the samples tested.

2. Make as many mixtures as you can with other tanning materials, run tests, and report mixtures taken and your ability to detect the two materials in question.

Digitized by Google

The chairman's object and desire in this work, was to find any and all weak points of the two tests in question, so that he could rectify them and arrange the tests to give general satisfaction.

Reports were received from only three members, Messrs. F. M. Loveland, F. P. Veitch and R. H. Wisdom, and the results obtained by them were very unsatisfactory on anything but pure materials. Also some apparently pure extracts which had received special chemical treatment gave negative results when positive results should have been obtained, and some materials gave some reaction in the test for hemlock when none was presumably present. It seems possible that different lots of the calcium chloride may have some influence.

With the mangrove test better results were obtained, but far from satisfactory. Attention of the chairman was called to a sample of mangrove extract which had received special chemical treatment and which gave only a very slight reaction. Also that some other extracts give slight reactions. Similar observations with this test were made by Stiasny and Wilkinson, *Collegium*, 1912; 509, 499, this JOURNAL, VII, 568, Oct., 1912.

The chairman wishes to thank the members for the work they have done, which co-operative work is very helpful in determining the reliability of a test under diversified conditions, and bringing out such features as require improvement.

Buffalo, N. Y., Nov. 6, 1912.

REPORT OF 1912 COMMITTEE ON ACIDITY OF TAN LIQUORS.

By Lloyd Balderston, Chairman.

Much has been written during the year on the subject of acid in tan liquors. Professor Procter, in his article in the *Shoe & Leather Reporter*, reprinted in the JOURNAL, for May, 1912, advocates for total acid, direct titration of the liquor without precipitating the tannin, the end point being determined by spotting out on hematin paper. He remarks that the acidity of pure tannins is so small as to be negligible. A sample of "pure tannin" which the writer examined by the electrometric method

Digitized by Google

showed a normality of 0.018 in a 1 per cent. solution. Tannin of this degree of acidity in a liquor having 5 per cent. tannin would neutralize 0.55 cc. of N/10 alkali for 3 cc. of liquor. To disregard the tannin in such a case would introduce an error of 0.11 per cent., if the acidity be expressed as per cent. acetic acid. Procter suggests congo red as an indicator for plumping acids, and the lime-water method for lime-dissolving acids.

H. G. Bennett, in the *Shoe & Leather Reporter,* April 18, 1912 (abstr. this JOURNAL, pages 382-385, July, 1912), reviews the various methods of determining acidity. The same writer in the *Leather Trades Review,* Vol. 45, pages 266-269 and 342-344, covers the same ground in somewhat different fashion, and adds some experiments comparing several of the methods. He used a modification of the lime-water method, diluting all liquors to 0.4 per cent. tannin content. By this means it is possible to compare the acidity of liquors in the same yard.

Mr. Bennett has done a lot of work with the lead-oxide method precipitating the tannin in dilute liquors (0.4 per cent. tannin) with lead-oxide digested in cold for a half hour and titrating with caustic alkali and phenolphthalein. The aim here is to obtain a filtrate containing lead salts of the plumping acids, lead acetate, formate, and lactate being soluble, while the gallate, sulphate, carbonate and oxalate are insoluble. Mr. Bennett expresses the hope that this method may be so developed as to give a reliable measure of the true plumping acids present. It would have to be taken in conjunction with an ash analysis to give any dependable measure of the plumping power of the liquor, since this power is diminished by calcium salts in solution, and these would not affect the result of the titration. No work has been done by the committee on the lead-oxide method.

Mr. Bennett remarks that the electrometric method does not measure the plumping power of a liquor, and since it estimates tannin, it does not correctly show the total acidity in the ordinary sense. Many determinations by this method have been made by Mr. Alsop and the writer. The total acidity as found by titrating 100 cc. of liquor with normal alkali to 0.69 volt as an endpoint, was always higher than that found by the gelatin-hematin method, and the difference was greater for liquors stronger in tannin. These differences are not exactly propor-

Digitized by Google

tional to the tannin strength, and seem to depend on the kind of tannin, as well as on the quantity. It may be possible to work out a table by which to reduce the results by this method to a standard form, showing total acid less tannin, when the kinds of tannin present in the liquor are known.

The process is not difficult to carry out, requiring about five minutes for a determination, and is applicable to other dark colored liquids, such as bleach liquors. Not enough data are yet in hand to warrant a positive statement in regard to soda solutions, but dark acid solutions can be titrated with ease and accuracy.

The papers of Wood, Sand and Law (this JOURNAL VI, pages 114 and 428), had led the writer to hope that the initial reading of the electrometric apparatus would give a measure of the plumping power of the liquor. It is not impossible that this hope may be realized, but if the initial readings are to give such an indication, some precautions must be necessary which we have as yet failed to discover. A set of determinations on liquors from one tannery varied in total acid (as acetic) from 1.09 per cent. down to 0.59 per cent. The initial readings varied from 0.47 volt to 0.51 volt. Thus a wide range in acidity is represented by a very small range in initial readings, and often with the same initial reading wide differences in total acid were found. Thus two liquors which gave the same reading at the start took 13.8 and 18.1 cc. normal KOH, corresponding to 0.83 per cent. and 1.09 per cent. acid as acetic.

G. Grasser, in *Collegium*, 1912, pages 57-58, (abstr. this JOURNAL, VII, 278, May, 1912), discusses some of the most used methods and recommends titrating with N/10 alkali using rosolic acid as indicator, after precipitating the tannin with gelatin. He uses a 4 per cent. gelatin, 25 per cent. salt solution, and heats the liquor to 40° C. with stirring, then filtering through loose cotton. The advantage of the strong gelatin solution over the 1 per cent. solution of our method is very slight, if any, and in no instance which has come under the writer's observation has the addition of salt made any appreciable difference in results. The filtration through cotton is inconvenient and offers no advantage over our method of taking an aliquot part of the supernatant

Digitized by Google

liquor. The writer believes that any method of filtration after gelatin is liable to involve loss of acid.

Several members were asked to test out rosolic acid as an indicator, and replies were received from C. C. Smoot III, W. G. Sprinkel and Max F. Woltz. Mr. Smoot and Mr. Sprinkel tested Grasser's method as compared with the ordinary gelatin-hematin method on a liquor whose acidity by the latter method was 0.75 per cent. Mr. Smoot's average by Grasser's method was 0.60 per cent., and Mr. Sprinkel's 0.64 per cent. Making up to 200 cc., filtering and titrating an aliquot part, both men got about 0.67 per cent. Making up to 250 cc., shaking with kaolin and titrating the supernatant liquor with rosolic acid indicator, gave Mr. Smoot 0.66 per cent. and Mr. Sprinkel 0.80 per cent. Hematin indicator on this liquor gave Mr. Smoot 0.60 per cent. and Mr. Sprinkel 0.61 per cent.

Mr. Woltz reports no figures, but says that Grasser's method gives lower results than the official method. This difference is probably due at least in part to the great excess of gelatin used.

To this committee was also assigned the subject of a proper preservative. Mr. Seltzer's article in the September JOURNAL recommends oil of mustard. Since this is volatile, the vessels must be closed, and the liquors not exposed to a high temperature. Since the chief loss of acid occurs in very warm weather, it seems to the writer not unreasonable to require that a preservative shall be efficient at 90° F. Mr. Seltzer also uses closed vessels, which would perhaps be inconvenient in tannery practice. Since thymol preserves the acid for two weeks at any temperature under 100° F. and does not evaporate, the writer regards it as a much more dependable preservative than oil of mustard. The chief objection to thymol is its cost, and the fact that if the sampler carelessly puts in too much, the analysis of the liquor will be spoiled. The proper quantity is only 0.02 per cent., affecting the analysis to a degree hardly appreciable, but if the sampler put in five times this amount, the total solids would be raised 0.1 per cent.

In assigning this topic the Council suggested that the preservative value of toluol be tested. Another material which came under observation is an antiseptic preparation called "chloronaphtholeum." The chairman carried out a series of tests on

Digitized by Google

these two substances at about 90° F. The toluol was entirely inefficient, and the other substance required ¼ per cent. to be efficient. This quantity has a decided precipitating effect on the liquor, which bars it.

A series of comparative tests at room temperature using toluol in varying proportions, $^1/_{20}$ per cent. oil of mustard and $^1/_{50}$ per cent. thymol was run with the result shown in the table. Liquor number 1 was almost pure oak; number 2 a blended liquor, 25 per cent. chestnut, 25 per cent. quebracho, 12 per cent. mangrove and 38 per cent. hemlock; number 3 a blend of 50 per cent. hemlock, 33 per cent. chestnut and 17 per cent. quebracho.

					Acid per cent. after 11 days				
Liquor	Degree bark.	Tannin per cent.	Nontans per cent.	Acid start per cent.	0.02 per cent. thym.	0.05 per cent. oil mustard	No antiseptic	0.05 per cent. toluol	0.10 per cent. toluol
1	35	4.2	4.2	0.79	0.76	0.78	0.31	0.36	0.36
2	23	3.2	2.3	0.39	0.38	0.36	0.18	0.16	0.16
3	20	2.8	2.2	0.43	0.40	0.36	0.18	0.14	0.14

These samples, 200 cc. each, stood in open vessels, at an average temperature of 20° C., and were made up to 200 cc. with distilled water at the end of the period. Neither those with oil of mustard nor those with thymol had any yeast-film at the end of the period. All the others had. Thymol and mustard oil were both quite efficient under these conditions, and the amounts of toluol used were entirely inefficient.

The chairman believes that the best method of securing samples from change is to have each sample as soon as drawn placed in a bottle, which should be entirely filled, and the bottle corked. If the cork is not too tight, there is no danger of bursting from expansion. Then at the expiration of the sampling period, all the bottles of which a composite is desired should be emptied into one vessel, thoroughly mixed, and a sample drawn for analysis, the bottle being filled and corked. If the sample must be shipped, of course it must be tightly corked, but in such a case the bottle must not be entirely filled. A small air space under the cork is no disadvantage if the time between drawing of the sample and its analysis is not more than three or four days.

That such bottling is a complete protection against loss of acid

Digitized by Google

has been repeatedly demonstrated. It seems to the chairman that the small additional labor in sampling would be amply repaid. The sampler would be much more likely to be able to carry out such instructions accurately than to use any kind of a preservative with uniformity and accuracy.

No method for total acidity has been devised which seems to us superior to the gelatin-hematin method as now used. Methods for distinguishing among the acids present are in such an early stage of experiment that we are not prepared to make any recommendation.

NOTES ON THE ESTIMATION OF FREE SULPHURIC ACID IN TANNERY LIQUORS.

By F. O. Sprague.

It is a point worthy of notice that many leather chemists are to-day bemoaning the lack of a method for the determination of free sulphuric acid in tannery liquors, when a method exists, which, in the hands of some operators, at least, has proven accurate and satisfactory. Parker and Payne[1] describe a method, based on the well known insolubility of sulphates in absolute alcohol. They place 10 cc. of tanning liquor in a 100 cc. stoppered cylinder, make to 100 cc. with absolute alcohol, filter, and determine sulphuric acid in the filtrate gravimetrically. The writer, a few years ago, gave this method a superficial trial, and had always considered it accurate; but of late some objections to it have been noticed, together with a general lack of knowledge of the existence of any such method. The only definite objection noted, aside from the fact that the water of the tan liquor is introduced into the alcohol, is, that in one case a definite amount of normal sulphuric acid had been added to the liquor, and none found by this method. The first objection is negligible. In fact, absolute alcohol is not necessary. As to the latter objection, the point immediately suggested itself, that perhaps not enough acid had been added, and that it had all combined with the lime present, setting free the organic or weaker acid. Not being an adherent of the creed that "the pen is mightier

[1] *Collegium*, 1904, 96.

Digitized by Google

than the test tube" an attempt was made to show that the slightest amount of sulphuric acid added, in excess of the amount necessary to replace the combined organic acids, would appear by this method.

Ten cc. of liquor were pipetted into a graduated, stoppered, cylinder, and made to 100 cc. with 95 per cent. alcohol, mixed thoroughly, and allowed to settle, when practical. The supernatant solution was then filtered, the first few cc. discarded and the sulphuric acid precipitated in the next 50 cc., heating on the water bath. The total calcium in the liquor was also determined and the amount of sulphuric acid necessary to combine with it calculated. No sulphates were found in the original liquors as no liquors from an "acid yard" were at hand. Normal sulphuric acid was added from a graduated pipette at the temperature at which it was standardized. The results appear in Table I.

TABLE I.

10 cc. solution	Grams H_2SO_4 added	Grams H_2SO_4 found	Unaccounted for	Grams H_2SO_4 calculated necessary to combine with Ca found present
$CaSO_4$	None	None	—	—
$CaSO_4$	0.1	0.096	—	—
$CaSO_4$	0.1	0.0112	—	—
5th layer	None	None	—	—
5th layer	0.105	0.087	0.018	0.015
5th layer	0.01	None	0.01	0.015
4th layer	0.0098	0.0006	0.0092	0.009
Tail rocker	0.098	0.075	0.023	0.027
Tail rocker	0.0098	None	0.0098	0.027

It will be seen that in the case of the tail rocker it is possible to add 0.5 cc. of normal acid without having any resulting free sulphuric in the liquor.

The total acid, determined by the official method before and after adding an amount of sulphuric acid less than enough to show any free acid, increases about the amount to be expected.

These notes are not offered as any original contribution to leather chemistry, but were undertaken in the course of regular work, as it was imperative to have an accurate method. The issue of *Collegium*, 1904, is out of print, so recourse to the original paper could not be had. It is probable that this ground has already been covered. The method is rather long to be

Digitized by Google

used in routine work where a number of determinations are to be made. Possibly a volumetric method can be devised for estimation of sulphates in the filtrate, but we are advised by Sutton[2] that "the determination of sulphuric acid in most cases is more easily obtained by gravimetric than by volumetric methods" and are then given many cases in which the latter are useful.

This method can be applied to many solutions, particularly lactic acid. [The directions for this test given by Parker and Payne in the article referred to by Mr. Sprague (*Collegium*, 1904, p. 95) are as follows: 10 g. of a liquid extract or tan liquor, or 5 g. of a finely powdered solid extract is placed in a 100 cc. stoppered cylinder, 90 cc. of absolute alcohol is added, and the whole well shaken. Filter through a dry filter, wash the residue with 90 per cent. alcohol and add the washings to the original filtrate, to which add 1 cc. conc. HCl and 2 or 3 cc. 10 per cent. solution $BaCl_2$. Filter, wash and weigh in the usual manner.—ED.]

SALT STAINS.

[We published in the November JOURNAL a general report of the London Congress of the I. A. L. T. C., Sept., 1912. The following discussion on salt stains is reported more in detail than in the account published last month and is taken from the *Leather Trades Review* for Oct. 16, 1912.]

Dr. Becker referred to the particular salt stains which he had discovered in his experiments. Those stains of various colors which have a destructive effect on pelt substance he considered to be the most dangerous; they were undoubtedly due to bacterial action as proved by his investigations, which were based on bacteriological facts. He was convinced that he was working in the right direction to trace those stains, and said the science of bacteriology played a much greater part in their raw material than tanners realized. He had discovered orange, yellow, bluish green and brown color bacteria in stained hides, and noted that from French hides and skins the stains were

[2] Volumetric Analysis, Tenth Edition, p. 349.

Digitized by Google

nearly always of a brown coloration. That was undoubtedly due to the tar used for denaturing the salt; not only did tar produce these brown stains, but it was of no use as a disinfectant. He said he had examined all these various stains under the microscope, and had noticed crystals of salt on the surface of the stains, which in every case were underneath the crystals. The subject of salt stains had created a great deal of interest, and he was glad there were now so many investigators endeavoring to trace every possible source of origin. The value of hides and skins susceptible to damage in Germany alone during a year amounted to M.80,000,000, and Dr. Becker added that he would gladly undertake to guarantee that no damage ever appeared on German hides and skins through this defect. Continuing, Dr. Becker said he had been able to produce yellow, orange, orange brown, and even blue stains by means of pure bacteria cultures. He had isolated those bacteria, and been able to produce those stains on gelatin. He had also succeeded in producing similar stains on pelts by inoculation, but it was more difficult than producing the stains on the raw untreated skin. He found that certain yeasts and bacteria were the actual cause of the damage, while the influence of salt had the effect of favoring the production of those stains; in fact, up to 10 per cent. salt on the weight of the material treated, he had found that the stains were more pronounced as the strength of the salt was increased. Alkalies assisted in the formation of those bodies, and, as decomposition was always going on, it could be readily understood that alkalies would help to produce those stains. The temperature of the raw hide store was also an important matter, and to obtain the best results it should be about 77° Fahrenheit. Beyond that point the higher the temperature the more pronounced were the stains produced. Dr. Becker congratulated Dr. Abt on his work, and stated that he regarded his research useful in that it dealt chiefly with the chemical part of the question, which, however, he thought a secondary matter to the bacteriological. The sulphates referred to by Dr. Abt were present in all crude salts, and were bound to have an influence on the color of some of those stains which were produced. (Here Dr. Becker handed round for inspection several of the cultures of bacterial stains which he had produced on gelatine, and the

Digitized by Google

various cultures were examined with considerable interest). Having shown how the stains were produced, Dr. Becker said that the next problem was to discover methods of prevention. The principal method of sterilizing bacteria was by means of heat, but that would be quite impossible, of course, in the case of hides and skins. Another useful method was by freezing, and could be applied in many slaughter-houses. Organic acids had a certain future before them, but the great danger was that by using those acids (formic, &c.) considerable swelling of the hide took place, so that it would gradually absorb water, and the tanner might find himself in the position of paying 7½d. per pound for water instead of for hide substance. Naphthaline, borax and etheral oils were to be recommended, and he was of the opinion that mustard oil in water solution was one of the best methods of disinfection. An American tanner named Schmidt had recommended the use of zinc chloride. He congratulated the tanner on this good practical suggestion, but the chemical was not suitable in all cases. Sublimate was also useful, but rather too dangerous for workmen to handle. Sodium bichromate, copper salts and similar metallic compounds had been used, but the only advantages of such substances were that they caused no swelling of the hide. Salt, if properly prepared and properly used, could be made almost a perfect curing agent for hides, provided it contained a certain quantity of soda. When using more than the necessary quantity of salt, bacterial life was developed, but when the same salt was treated with 3 to 4 per cent. of calcined soda, bacterial growth was arrested. Another point to observe was that crystallized salt should not be used, as the danger of stains was considerably minimized by using powder salt. The latter, could also be used on the hair side as it would gradually disappear from the surface of the skin, but the cost would be greater to the tanner, although the skin would be better preserved. It was significant to find that certain stains on hides were more pronounced in some districts than in others, but after careful investigation he had established the fact that stains were both larger and more frequent on the hides from those slaughter-houses which were kept in a dirty condition, and where salt was used over and over again. Another frequent cause of stain was due to salting the hides immediately after tak-

Digitized by Google

ing them from the animal's back. In every case they should be allowed to cool thoroughly before salting, otherwise the natural heat of the skin favored bacterial action. Dr. Becker insisted on cleanliness in slaughter-houses, because not only salt stains but dirt containing bacteria had a liquifying action on hide substance, the loss of which in addition to the danger of salt stains ought to be avoided. Fresh salt should be used in every case. The slaughter-man's hands ought to be kept as clean as possible, the abattoirs should be constantly cleaned, while finally the cellar or department in which the skins and hides were stored should be kept cool. He had to admit that the presence of soda was attended with a little danger; if used in the slightest excess, or if allowed to remain on the hides it was liable to make loose leather. He would strongly recommend that all hides preserved by the soda-salt process be first softened in water for a short time. Dr. Becker said finally that the subject of salt stains ought to be taken up energetically, and with that object in view he favored the immediate appointment of a commission to fully investigate the question.

Dr. Abt said that in dealing with the question of salt stains the first thing to ascertain was the class to which they belonged. He was convinced that there were several classes of stains which were of quite distinct origin. He had discovered that one class of stains was caused by small grains of calcium sulphate in the salt used for preserving the hides. Those grains were of the size of about 1 to 3 mm., and easy to find in many salts. The first salts that he experimented with contained more than 4 per cent. of calcium sulphate. If the calcium sulphate were present only in its pure form it would not matter, because it would remain in hides and skins as a soluble salt; but it was found that calcium phosphate was formed, due to the action of sulphate on the nucleic acid in the skin. The origin of the stains in that case was the small particles of calcium sulphate. Dr. Becker, on the other hand, had been successful in finding quite another class of stains, and he was confident that they were quite different in character to what he had found. What he had studied were skins with grey and sometimes marbled markings, and he found that these eventually turned black if they came into contact with iron sulphate. When washed with dilute

Digitized by Google

acid the color would gradually disappear. He had also found yellow and brown colored stains. When skins marked in that way were placed in tan liquors the color changed to dark brown, sometimes almost black. In those particular cases he felt sure the stains could not have been produced by bacteria. Another point was the question of the loss of hide substance. He had made experiments in that direction, taking pieces of skins that were stained and some that were not stained, and had found no difference as regards loss of hide substance. He had tried to stain the microbes in the grain, but had never been successful. He was of opinion that if bacteria were found on the grain they would have passed through from the flesh side. He had not been able to cultivate bacteria on the grain. Calcium phosphate stains on hides were particularly shown in lime liquors, where the hides frequently turned black owing to the formation of iron sulphides. Sometimes stains were removed if the hides were treated with lactic acid. Skins which had been badly taken off, and those which had a lot of blood in them, were particularly liable to stains, but the main point was to know the special class of stains that were being dealt with, so that the necessary chemical analysis could be made. If there was no calcium phosphate there was no need to look for that reaction. Dr. Abt said that it would be extremely useful if Dr. Becker could definitely ascertain the class of stains he had studied, as he thought that classification was a very important point. A case had come to his notice where a firm had had considerable trouble with salt stains until about two years ago, since when they have had no trouble at all in that direction. The firm was unable to state the exact reason for the change, but they attributed it to the mixing of two kinds of salt which they had used at different stores. The addition of soda would undoubtedly improve many kinds of salt for preserving hides. Dr. Abt thought that soda had not been sufficiently tested with salt containing a lot of sulphates. It was possible that soda had an antiseptic power and also acted as a dehydrating agent, but in actual practice some firms had made objections to the use of soda.

Professor Procter said he would like to raise two points as an old tanner and chemist. He fully agreed with Dr. Abt that there were two or three classes of salt stains. When a tanner

Digitized by Google

he had used South American hides, and at that time what were known as salt stains were usually of a pale yellow color, hardly visible in the raw hides or skins, but which became darker in later processes. Chemical examination showed that in all those cases iron was present. In later processes these stains often disappeared, but not always. Another kind of marking to which he was accustomed was a marbling discoloration, and so far as could be ascertained in those days there was no bacterial destruction and no damage on the surface of the hide. What Dr. Becker understood by salt stains was quite another class, and required very careful examination. A tanner once consulted him about some kips that had been badly stained; not only was there trouble with the stains, but the liming was extremely slow and unsatisfactory. The stains were no doubt due to the kind of plaster—a salt earth—that was used in preserving Indian kips. That earth contained silicate of soda, sodium sulphate with small quantities of potassium carbonate, and traces of iron. Even these impurities would not have stained the leather, because the iron was in the form of an oxide, and therefore insoluble, but after the leather had been kept in a London warehouse or in a damp store-room the iron in the earth acted upon the hides and stained them. This was due to the effect of carbon dioxide and moisture, which converted the salts in the plaster into a soluble bicarbonate. The latter penetrated the fibers and caused bad stains. In regard to the question of using organic acids as antiseptics, he pointed out, in reply to Dr. Becker, that such acids swelled the hide, consequently the tanner would have to pay for extra weight if the acid were used alone. On the other hand, if the acid were used in conjunction with salt, as had been suggested in some processes, notably in the formic-mercury process, the hide was not finally swollen, but, on the contrary, dehydrated, so that it would probably weigh less than in its original condition. In my article "Swelling of Acids" I took gelatine as a prototype, and experimented on a piece of gelatine which absorbed 51 times its weight of water in hydrochloric acid. If this same piece of gelatine were put into a salt solution of some strength a strong dehydrating effect would be shown; in fact, the mass would be made perfectly hard and horny. Therefore, if a tanner preferred to have the skins preserved by the use of

Digitized by Google

formic acid, he should demand that salt be used afterwards, so that he would not have to pay for water. Organic acids could thus be used in such a way that there would be less water in the hide than when first removed from the abattoir.

Dr. Lindenhayn said that conclusions ought not to be drawn up too quickly in this important matter of salt stains. Since Professor Becker had isolated a few bacteria it was more than likely that several other bacteria would eventually be found in hides cured in a different way to those that Dr. Becker had examined.

Dr. Andreis then related an interesting practical experience. Some time ago he had several thousand hides to export to England, and they had to be cured according to the order of the British Government. It occurred to him that instead of placing the hides in a brine pit, and then hanging them up to dry, there would be less likelihood of salt stains and other damage if he placed them over a specially constructed horse. By the latter method all the blood, dirt, and other impurities likely to set up bacterial action were drawn off, and the hides undoubtedly made very much more perfect leather. Unfortunately, the hide merchants lost about 20 per cent. weight as compared with 8-10 per cent. by the pit system, so that the method did not become popular. He suggested that if alkalies were useful in conjunction with salt to prevent salt stains he would favor alkaline preparations.

Professor Baldracco referred to some research work he carried out some time ago. From these tests he was able to state that by the use of 1 per cent. of sodium fluoride on the weight of the salt used the danger of salt stains was entirely eliminated.

Mr. C. E. Parker said he would like to say a word or two on behalf of the tanners present. Thanks were due to Dr. Becker and Dr. Abt for bringing up the subject in such an interesting way. The discussion has revealed a very difficult proposition. Professor Procter had said, when discussing the acidity of liquors, that it might not be an interesting subject to us as tanners. He thought that some of the tanners had learned what a difficult question the subject of salt stains was, and he said

Digitized by Google

they were prepared to wait until the matters had been studied further by chemists and something definite and practicable put before them. The danger in the past has been that many chemists had placed before practical men undigested scientific proposals which has not only caused loss to the tanner, but had also brought some discredit on the application of science to their trade. Speaking on behalf of the tanners, he said they all hoped that the chemists would arrive at a satisfactory settlement of the question of salt stains.

Mr. J. T. Wood remarked that although the salt used for preserving hides and skins in England was practically pure and had not to be denatured for industrial purposes as in several Continental countries, there were many cases of salt stains in this country. He thought that Dr. Becker and Dr. Abt were probably correct, and the action in both cases would appear to be similar, but no one appeared to know definitely what chemical reactions actually took place after the salting process. Dr. Abt had pointed out that probably neither bacteria nor the products of bacteria had caused stains on the hides and skins he had examined, because he had not found bacteria on the hair side of hides, and he failed to see how products of bacteria could reach the hair side. Mr. J. T. Wood pointed out that by the phenomena of osmosis it was not difficult for bacterial products to go through the hides to the grain or hair side.

Mr. Seymour-Jones desired, as chairman of the International Commission for the Preservation, Cure, and Disinfection of Hides and Skins, to congratulate Professor Becker and Dr. Abt on the work they had done. He had frequently discussed the matter with Professor Procter during the last 25 years. He said that the damage caused by bacteria could be largely avoided by thoroughly cleansing slaughter-houses, whitewashing the walls at regular intervals, but more particularly by disinfection of the hides. As a member of the Local Government Board in the county of Denbigh he had to see that these precautions were taken. One of the most prominent Governments in the world—he would not say which—intended to go very thoroughly into the scientific preservation and sterilization of hides and skins, and he thought they would take action from the results of their de-

Digitized by Google

liberations. The question largely resolved itself into a matter of purity of salt and the subsequent use of a suitable antiseptic. It must not be overlooked that bacteria played a big part in the question, and he hoped that a committee would be formed to further carry on the work of investigating the question of salt stains.

Dr. Parker hoped that the work would be carried on until all possible causes of stains were discovered, and suitable preventives applied.

Professor Becker, replying to numerous questions that had been raised, and to some inquiries that members had submitted to him on paper, said that the appearance of greenish stains he had referred to were due to a mixture of blue and yellow. The reason why stains were very frequent in wet-salted skins was that bacterial action was increased in dampness. Dr. Abt. had succeeded in producing another class of stains, and he thanked that gentleman for pointing them out. He was quite certain of the stains he had investigated, however, as he had been able to produce them both on pelt and on gelatine. He had not succeeded in finding any other stains than those he had already referred to, although he had examined both German and French skins. He said that bacteria were even more international in character than people. He had been unable to produce the stains with gypsum. The iron stains were due to bacterial action on the blood which contained iron. In certain bacterial action iron was transformed so as to give iron stains which were different to the salt stains he had tested. As regards sodium fluoride, he was well acquainted with that preservative, the action of which proved that the real cause of salt stains was bacterial activity. He thought it would be an excellent plan if tanners would test the soda-salt preparation and give some information of their practical experiences with this mixture. If they found the test satisfactory they could demand that soda-salt be used. He did not altogether agree with the method of curing suggested by Mr. Andreis, and there were several other points he would like to have referred to if time had permitted.

Digitized by Google

TANNING SCHOOL AT BARCELONA.

The ancient city of Barcelona, near the northern extremity of the Mediterranean coast of Spain, has long been an important industrial center. In a recent number of *Le Cuir* is a brief note recording the establishment at the Industrial University of Barcelona of a school of tanning under the direction of Doctor Ettore Giusiana, who will be professor of the chemical technology of tannage at the University. The new school is under the auspices of the Spanish government. An experimental tannery equipped with the most modern machinery and appliances is being provided, and students will have at their disposal the great laboratories of the University. The high reputation of the director is a happy augury for the success of the new school.

ABSTRACTS.

Study of Some Tanning Materials of Belgian Congo. A. PIRLOT. *Bourse aux Cuirs de Liége,* through *Le Marche des Cuirs,* Vol. 24, 1912, pp. 480 and 501. The work outlined was done by Messrs. Nihoul and Sody at the Liege Tanning School.

Terminalia Catappa.—The bark of this tree is from 4 to 5 mm. (0.16 to 0.2 inch) thick. By the filter-bell method, this bark shows a tannin content of 24.4 per cent., non-tans 4.8 per cent., moisture 13.8 per cent. The liquor, tested by the Lovibond tintometer showed 3.9 red and 8.7 yellow. With ferric alum, a blue-black color is obtained, and with bromine water a brown precipitate. The tannin, therefore, belongs to the catechol class. Stiasny's formaldehyde-hydrochloric acid test confirms this classification. A color test on goatskin gave reddish leather. Decolorization was attempted by boiling with malt, but although filtration was rendered easier, the color was redder than at first. A second attempt employed aluminum sulphate and sodium bisulphite. The aluminum hydroxide produced by the reaction helped the filtration. The liquor before treatment showed tannin 24.3 per cent., non-tans 4.7 per cent.; after treatment, tannin 22.3 per cent., non-tans (yellow) 10.8 per cent. Tintometer test showed 2.5 red and 6.1 yellow. Color test on goatskin did not show the reddish tint before observed.

Bempanza Bark.—By the filter-bell method this material gave 11.6 per cent. moisture, 12.8 per cent. tannin and 3.7 per cent. non-tans. Tintometer test showed 5.8 red, 15.3 yellow. The bark is easily extracted and the infusion easily filtered. L. B.

Digitized by Google

A New Process of Liming. E. GUISIANA. *Le Cuir*, V, 639, Oct. 1, **1912.** The method is adapted for hides intended for chrome tannage, possessing the advantage that the unhairing may be accomplished without swelling, which is an injury to skins having a fine uniform grain. A paste of sulphide of sodium applied to the grain splits into sodium hydroxide and sodium hydrosulphide, according to the equation $Na_2S+H_2O=NaOH+NaHS$. The hydroxide swells the skin and the hydrosulphide unhairs it. Sodium chloride will prevent swelling, and will do it the better if produced in the reaction. Dr. Guisiana has devised a depilatory consisting of sodium sulphide and calcium chloride in the proportions necessary to fulfil the following equation, $2Na_2S+2H_2O+2CaCl_2=4NaCl+Ca(OH)_2+Ca(HS)_2$. This liquid unhairs without swelling. If swelling is desired, it may be obtained by diminishing the proportion of calcium chloride. Good results are obtained by substituting for calcium chloride the chloride of ammonia, magnesia or barium, the reactions being precisely similar to that in the case of calcium chloride. The ammonia and magnesia mixtures give a very soft fine grain. Commercial sodium sulphide is 60-65 per cent. pure. In the following formulas the commercial sulphide is meant.

	For 100 lbs. green hide		For 100 lbs. dry hide	
Water	92	gallons	120	gallons
Sodium sulphide	3	pounds	5	pounds
Calcium chloride cryst.	5.22	pounds	8.7	pounds
or Magnesium chloride cryst. ..	4.83	pounds	8.05	pounds
or Ammonium chloride cryst...	1.26	pounds	2.10	pounds
or Barium chloride cryst.	5.89	pounds	9.65	pounds

Such a bath may be used a second time, adding half the quantity of each material at first used. L. B.

The Decolorization of Tanning Extracts by Means of Metallic Resinates. E. GUISIANA. *Le Cuir*, V, 611, Sept. 15, **1912.** Colored metallic resinates soluble in benzine, etc., are used to dye, and at the same time render impermeable, leather, silk and fabrics. They are easily prepared by coloring resin soaps with aniline dyes resistant to the action of acids and alkalies, and then precipitating these soap solutions with metallic salts. The resin soap is prepared by boiling rosin with sodium carbonate in the proportions indicated by the equation $C_{44}H_{62}O_5+Na_2CO_3=C_{44}H_{62}O_5Na_2+CO_2+H_2O$. One hundred pounds of rosin require from 15 to 18 pounds of dry sodium carbonate. These are boiled in plenty of water for 3 or 4 hours. The aniline color desired is then added and the solution precipitated with a salt of barium, zinc or aluminum. The precipitate carrying down the color is received on a cloth filter, washed with hot water, dried and dissolved in benzine, or in a solution of rubber in benzine. Dr. Guisiana applies this process to the clarification of tanning extracts as follows: To a liquor of 3 to 4° Bé, of chestnut, mangrove or spruce,

Digitized by Google

an amount of rosin soap is added equivalent to 5 grams of rosin per liter of liquor. On heating to 80° C. a persistent cloudiness is observed. Mix well and add a metallic salt, *e.g.*, zinc sulphate, slightly acidulated with lactic or acetic acid. A precipitate forms which may be separated by filtration, after which the decolorized liquid may be concentrated. The quantity of zinc sulphate added is from 0.8 to 1 gram per liter. The decolorization is very marked. Dr. Guisiana has not determined the loss of tannin, but believes it to be very small. He invites those interested to experiment with the method. L. B.

Lactic Acid for Drenching. *Hide and Leather.* In using lactic acid in the drum for bating sheepskins, sufficient water must be carried or the stock will take on a brownish hue. This is not detrimental if a wool-puller is a tanner, but if he sells his skins in the pickle they look bad. Lactic acid, used as it should be, takes the place of the bran drench on most classes of stock, and is always under control. Lactic acid should be free from iron and a sulphuric acid, as such substances are very injurious to green hide.

Sugars are contained in many vegetable products, and, through the process of fermentation, lactic acid is developed. Years ago, the old-time tanner knew that his first liquors must be a little sour or his green hides would not plump. It was lactic and acetic acid developed by fermentation of the non-tans of the hemlock bark that plumped the hide.

To-day, extracts are mostly used for tanning and it is necessary to add a certain amount of commercial acid to sour the first liquors. It was the fermentation of the bran drench that brought out this lactic acid that killed the lime. In this bran drench there was a bacterial action as well as chemical.

In using lactic acid alone no bacterial action takes place; therefore, if a tanner is looking for weight in his leather, lactic acid without any bacterial action is needed. Lactic acid may be used in pits for skins the same way as bran, but there will be no rising of the skins, consequently the skins must be moved or colored patches will show and the skins will not be evenly drenched.

Notes on Goatskin Leather. *S. & L. Rep.*, Nov. 7, 1912. There are several ways to unhair goatskins. They can be unhaired by being limed in clean white limes or in limes containing either red arsenic or sulphide of sodium, and they can be painted with a mixture of lime and arsenic, unhaired and then limed in a paddle wheel in a lime containing some red arsenic. In the last named process the skins are soaked until they are soft and are then washed and placed over horses to drain over night. Some sulphide of sodium or caustic potash should be added to the water in which they are soaked to hasten the softening and freshing of the grain. Two or three days before it is used a mixture of lime and red arsenic should be prepared with which to paint the skins.

Digitized by Google

Prepare the mixture as follows: Mix in a suitable tub or vat one hundred pounds of lime and six pounds of red arsenic. Pour on sufficient hot water to thoroughly slake the lime and make a paste of the consistency of paint. The mixture should be thoroughly stirred and allowed to age before it is used. The skins are spread upon a table one at a time and are painted upon the flesh with a thick mixture of paint and arsenic, folded down the center and placed in a vat until the vat is about two-thirds full. The skins should be weighted down with boards and stones; and the vat should be filled with water. At the end of five days, and not infrequently four days, the hair can be easily removed and the skins placed in lime in a paddle wheel for further liming. All short hairs that may be found on the skins should be carefully removed.

The lime solution for the vat is prepared by slaking twelve pounds of lime and four pounds of red arsenic for one hundred pounds of skins, using one-half of the mixture at first and adding the rest the next day. After three or four days the skins are removed from the lime, washed and fleshed. When they have been fleshed they are washed in warm water for a few minutes and are then placed in the bate. The most satisfactory process of bating goatskins is by using a bacterial bate. There are good bates on the market that are cleaner and safer than dog excrement, which is an effective bate but disagreeable to handle. The skins should be bated until they are soft and silky, then removed from the bate and scudded, and then washed again in warm water containing a small quantity of boric acid. The next operation is pickling, which can be done with sulphuric acid and salt or with formic acid and salt.

The latter process has some advantages over the former. Pickling is done most expeditiously in a drum, the skins being drummed in the solution of salt for a few minutes and the acid being then added. From the pickling drum the skins are drained a few hours and are then passed into the first bath of the chrome process, which may consist of bichromate of soda and muriatic acid or of chromic acid and dissolved in water. The two-bath process is so well known that it is not necessary to describe it in this article. When the skins are thoroughly leathered they should be placed smoothly over horses and allowed to press and drain for a few days. It is not good practice to wash them as soon as they are tanned. At the end of three or four days, wash the leather in hot water in a drum or twister, drain and then shave it to uniform thickness, then neutralize the remaining acid by washing in warm water containing one pound of sodium phosphate for one hundred pounds of leather and then again washing in warm water in the wash wheel. The next process is coloring. If the leather is to be dyed black good results can be obtained by using logwood and titanium potassium oxalate or logwood as a bottom color and topping with direct chrome black. There are excellent dyes obtainable at the present time that produce fast shades that are richer and deeper than the dyes formerly in use. They are generally applied upon a tannin mordant. An excellent fat liquor is made of neatsfoot

Digitized by Google

oil and egg yolk added to the waste dye bath. When the fat-liquoring is completed the skins should be dipped into hot water to remove surface grease, drained over night and then set out on the machine and receive a coat of glycerine and water followed by an application of oil, either sperm or neatsfoot, and then hung over poles to dry. When dry the leather should be left in a clean, dry room for some time before it is finished.

Dull finished leather is usually given more oil than glazed in order to give the grain the soft, silky feel. If a dry feel is wanted the leather is given a lighter coat of oil, some tanners using a special kid finishing or mineral oil for the purpose. To remove the grease from the grain before applying the seasoning for glazed finish, use either benzine or a solution of lactic acid and water. Rubbing the grain with a sponge or a rag dipped in benzine is a good way to rid it of surface grease. The writer considers it of help to tack the skins after the last staking and while still damp upon boards to make them flat for finishing. After the last glazing, some finishers apply a light coat of finishing oil to the glazed surface to preserve the finish and make it more waterproof.

In every stage of the process of tanning goatskins care must be taken to get a smooth grain and to avoid the use of anything that will make the grain coarse or rough before it enters the first chrome bath. The use of a small quantity of caustic potash in the soaks, painting with lime and red arsenic as described and then liming for a few days, bating with bacterial bate and tanning with the two-bath process are some of the secrets of making fine, high-grade and salable dull or glazed goat leather.

How to Tan Goatskins by the Two-Bath Chrome Process. *S. & L. Rep.*, Nov. 7, 1912. Good chrome leather can be made by using chromic acid in the first bath of the two-bath process instead of bichromate of potash and acid. This part of the process is best carried out in a drum in the following manner: Weigh the previously pickled skins and for each hundred pounds of them use four pounds of chromic acid and five pounds of salt and fifteen gallons of water. Dissolve the acid and salt in a few gallons of the water and add the solution to the rest of the water and drum the skins in the liquor four hours, then place them smoothly over horses until the next morning, taking pains to cover them so that no parts will be exposed to the light. The next day strike the skins out on the machine and put them into the second bath.

When bichromate of soda or bichromate of potash is used the usual formula is six pounds of the chemical and three pounds of muriatic acid for one hundred pounds of skins. If a drum is used fifteen gallons of water are used for one hundred pounds of skins; when a paddle is employed sixty gallons of water are required. It is immaterial whether bichromate of potash or of soda is used; the results are the same. The bichromate of potash or soda is dissolved in boiling water and the solution is poured into the water in the reel, the acid is then added and the

Digitized by Google

bath allowed to stand a few hours before the skins are put into it and then stirred well before the process is begun. The stock should be paddled in the liquor several hours and then left in over night, stirred up well in the morning, taken out and struck out.

The second bath may consist of either bisulphite of soda or hyposulphite of soda and muriatic acid, with the advantages in favor of the former as it costs less and there is no sulphur formed in the liquor. It is advisable to use more hypo or bisulphite than the skins require since they absorb only as much as they require and it is better to have an excess rather than a deficiency. Fifteen pounds of hypo or bisulphite and six pounds of muriatic acid produce good results in the second bath. The soda is dissolved in a tub and added to the water in the vat, two pounds of acid are added, the liquor stirred for a few minutes and the skins thrown in.

After the skins have been paddled for ten minutes two pounds more of the acid are added and one hour later the third portion of two pounds is added after dilution and the paddling is continued for three hours or until the yellow color has entirely disappeared from the center of the thickest skins and the goods are a uniform green color throughout. It is very important that the reduction is thorough and for this reason it is advisable to leave the skins in the bath over night and then to paddle them one-half hour the next morning. It is also beneficial to the quality of the finished leather to keep the leather horsed up a day or two before washing, shaving and neutralizing it. It is important that the acid that is used be of uniform strength, which should not be less than 20° Baumé. Such impurities that are found in the acid are of no consequence to the tanner. The carboys should be kept securely closed so that none of the gas can escape. Sulphite of soda is used by some tanners to reduce the amount of sulphur developed in the second bath, while others use no hypo at all, employing bisulphite of soda instead with equally good results without the obnoxious sulphur.

To prepare the leather for shaving, wash it in hot water in a drum, giving it two changes of water and washing it at least one hour. After the leather has been washed it should be drained, shaved and then neutralized with washing soda and chloride of ammonia in warm water. For each hundred pounds of leather dissolve two pounds of washing soda and two pounds of chloride of ammonia in warm water and add the solution to the water in which the skins are to be washed. Wash the leather in this water for ten minutes, then run off the water and add fresh containing like the first two pounds of washing soda and two pounds of chloride of ammonia. Washing fifteen minutes longer thoroughly neutralizes the leather so that it can be colored, fat-liquored and finished with no danger of spewing. Before proceeding to tan the skins after they have been puered and washed, pickle them with four pounds of sulphite of alumina and six pounds of salt for each one hundred pounds of skins; ten or twelve gallons of water being used and the

Digitized by Google

process performed by running the skins in a drum for one hour. Pickling helps to make the soft, fine grain that is required on goatskin leather at present. The common pickle of sulphuric acid and salt also can be used, also formic acid and salt. The above described process of tanning produces leather that can be colored, fat-liquored and finished into good, salable stock, provided the skins have been limed and puered properly in the beamhouse.

The Purification of Tannery Effluents. LOUIS MEUNIER. *Collegium*, 1912, p. 268, through *Leather Trades Review*, Oct. 16, 1912. Different methods which have been used in the disposal of general city sewage are discussed. In approaching the problem of tannery effluents, the author proposes several preliminary questions, and concludes, (1) that purification is not necessary where the effluent is discharged into municipal sewers, or into large rivers; (2) if the volume of the stream receiving the effluent is about 50 times greater than the volume of effluent, partial purification is sufficient; (3) where complete purification is necessary the spreading or irrigation system or bacterial beds must be resorted to. Which method shall be used in the last case depends on the situation of the works. Detailed studies of the effluent from one small sole leather tannery and its effect on the stream into which it flows, are given. Prof. Meunier concludes that it is advantageous to mix the various residues after the solid matters have settled out.

Leather for Bookbinding. *S. & L. Rep.*, Nov. 7, 1912. Among the many tannages that are suitable for shoe and fancy leather there are only two or three that can be used in making leather for the purpose of binding books. Pure sumac and pure oak bark are the most suitable and least injurious to the finished leather. The use of acids in any stage of the process is dangerous as it tends to weaken the fibers.

The leather must be tanned without acid and it must be firm and dry and have a natural smooth grain, except morocco which has a pebbled grain. The leather must be tanned in such a way that it will have a clear, light-colored grain that will not require bleaching, since bleaching invariably injures the fibers. If the leather is to be colored, only such dyes that do not require acid for their development can be used. Aniline dyes can be used but they must be used without sulphuric acid.

When the desired shade can be secured by using dye-woods they should be used in preference to aniline dyes. Chrome tanned leather is not considered suitable for book-binding although when tanned without acid and finished dry and firm such leather has great durability, and, it would seem, is more suitable than vegetable tanned leather. Quebracho, myrobalans, chestnut, etc., are not considered as good as the pure oak and sumac tannage. The color need not penetrate through the leather but should be fairly uniform upon the surface. The most durable leather is that tanned with oak or sumac, dyed with dyewoods or non-acid

Digitized by Google

aniline dye and finished without grease and with a natural smooth grain. Leather with an artificial grain is quite unsuitable.

If undyed leather is wanted a good color is obtained by tanning in clean liquors; there are also dyes that can be used that improve the natural color of the tannage without injury to the strength or durability. One process of dyeing the leather a dark tan consists in drumming it in a solution of fustic extract, red shade, thirty minutes, then pouring into the drum a solution of titanic salts and drumming the leather fifteen minutes longer, washing and finishing it. Russet sheepskins for bookbinding must be free from the natural grease and acid and have a good color and fine, smooth grain. Calfskins tanned with oak make splendid bookbinding leather, that can be easily colored any desired shade. Such leather is more durable than sheep leather and presents a richer appearance.

Fundamental Rules of Practice. II. Vegetable Tanning Liquors. L. MANSTETTEN. *Ledertechnische Rundschau,* IV, pp. 298-300 and 321-25. (Previous instalments abstracted in Vols. V and VI, *J.A.L.C.A.*) The make-up of liquors is one of the most important problems in modern tanning. The tanning value of a material depends on the amount of tannin present and on its character, on the influence of non-tans present, and on the behavior of the tannin during leaching and in the yard. About 30 pounds of tan are contained in 300 pounds of pine bark or in 100 pounds of mimosa. Assuming that 20 per cent. of the pine is leached out, and 40 per cent. of the mimosa, 240 pounds of pine bark remain and 60 pounds of mimosa. If 3 per cent. of tannin remains in each after leaching there is a loss of 7.2 pounds in the pine and 1.8 pounds in the mimosa. Taking the average prices of these materials, this loss amounts to 50 cents on 300 pounds of pine bark and 13 cents on 100 pounds of mimosa. Thus the price per tannin unit shown by analysis to be in the raw material does not alone show how much a unit of tannin in the liquor will cost. Eitner (*Gerber,* 1907) has shown that old pine bark contains a larger proportion of difficultly soluble tannin, which will be deposited in cold liquors. This source of loss must be reckoned with. Paessler and Veil (*Gerber-Zeitung,* 1908) showed that the best utilization of tannin is realized in general in weaker liquors, although in some conditions stronger ones are equally advantageous. It is better in using extract to dissolve in warm water. The tanner can use untreated quebracho to better advantage than the more costly treated extracts if he knows how to make the insolubles available. This may be done by proper treatment in dissolving, or by using warm liquors. Some liquors suffer loss of tannin on standing. Myrobalan liquors have been known to lose as much as 30 per cent. of their tannin in 15 days. Divi divi and knoppern also suffer serious loss. Materials which settle from valonia, myrobalans and divi divi liquors are desirable in the case of some leathers. If the leather is to be dyed, however, such bloom deposits must be removed,

Digitized by Google

or irregular color will result. Eitner (*Gerber*, 1907) published observations on the colors imparted to leather by different tanning materials, and the changes which these colors undergo by exposure to light. More important than the color produced by a tanning liquor is its actual tanning effect. In order to arrive at an opinion on this point, the tanner must know the composition of the liquor and the kind of effects produced by each component. Materials present in a liquor are usually classed in the three groups, tannin, acid, non-tans. The last may be divided into sugars and other things. From the fermentation of the sugars come the so-called natural acids of the liquors. The tanning effect of a liquor depends on three things, (1) the kind of tannin present, and the kinds of acids; (2) the percentage of tannin and of acid, and the ratio of these to each other; (3) the proportion of both these quantities to the quantity of non-tans. A liquor having much tannin and little non-tan tans more strongly and is less suitable for the early stages than one with the same amount of tannin and a larger proportion of non-tans. In general, a large proportion of non-tans causes slower tannage and softer leather. If the earlier liquors exert too vigorous a plumping effect, salt may be added to check it. The question how to prepare a liquor suitable for a given purpose is not easy to answer. Experiment and observation are the only safe guides. The practical value of the barkometer is often overestimated, and that of chemical examination underestimated. The barkometer gives no dependable information unless the components of the liquor are known. A fresh liquor of 6° Bé. may have an even greater tannin content than an old drum liquor of 8° or 10°, because of the accumulation of non-tans in the used liquor. If the proportion of tannin to non-tans in the extract or other material from which the liquor was made be known, the specific gravity of the fresh liquor may be used to calculate its tan content. Details are given in regard to the preparation of blended liquors to contain various proportions of tan, non-tan and acid or acid-forming sugars. The disadvantage, for most purposes, of running spent liquors back over the leaches, is emphasized. When a liquor of 1.5° Be. is thrown away as used up, it would appear to contain no available tannin, and analysis would show almost none, yet such a liquor may be well adapted for the first stages of tannage, which really involve mainly surface effects. The writer strongly recommends the method of tannage in which the liquors work down as the hides pass up, thus automatically adapting themselves to each step of the tannage if they have been properly prepared in the first place, and are run away at the end of the series. Drum-tannage or other method which cannot conveniently use such a series of liquors presents serious difficulties because of accumulation of non-tans due to strengthening of the liquors. L. B.

The Tanning Experts of To-day. *Gerber*, No. 912, Sept., 1912. In former times leather experts wandered from tannery to tannery with

Digitized by Google

patents, advice, etc., and offered them for certain remunerations; these were men who previously had themselves been manufacturers but had become financially embarrassed. Others in this business were tanners who wandered about among different tanneries and who were believed to have learned something here and there; others still were swindlers who defrauded wherever they could and who obtained their knowledge from receipt books, etc. While the early tanners were especially conservative yet, if approached in the right way, they could be induced to try new methods. However, though many of the new changes suggested by these men were rejected, several serviceable things remained which were, in reality, changes for the better. Through the failure, too, of many new methods prejudice against radical changes increased and, curious to relate, this prejudice remains only toward progressiveness. The class of experts during the present day have assumed a modern form which must be reckoned with since too much importance is attached to them. At the present day in place of the visits of these wanderers, the tanner is assailed with all kinds of circulars from people who profess to be doctors or professors of tanning. There are now so many of these self-styled experts that steps should be taken for protection from them because, while a few are of benefit to the tanner, many more are a positive injury. It is suggested that a commission be appointed to consider the processes offered and that the results of experiments be made known. Data could thus be gathered together at some central location and given out upon inquiry. At first it was the extract tanning expert and then the drum tanner who found a rich field among the many who turned to these methods. The repugnance of many tanners to innovations has been due to the fact that those demonstrating the new methods have little practical experience and might do serious injury to stock. On this weakness of the tanner the modern tanning doctor, engineer or chemist has built up the right to exist. The idea of entrusting the trial of a new method to one who is thoroughly acquainted with it is far more reasonable than for the tanner to leave the same to those who have not practical experience. Much will depend in any case on the quality of the instructor chosen. The great opportunity for the activity of experts of this kind arose when the new extract and drum tannages came into vogue. In the earlier years these men were largely tanners, foremen, workmen or pretenders who obtained their knowledge from practical experience, from reading and from experiments which they had tried or seen tried by others. By the success of these experiments accomplished at the cost of others the expert plays a winning game. Some of these experts gain admittance to works for the sake of spying, either being hired by others or trying to obtain something for their own utilization. Others in this line travel between Europe and America and sell on one side the things they have learned on the other. The one great field for tanning experts is tanning for weight. Inventors of such processes generally produce their own materials and send out instructors who teach the correct use

Digitized by Google

of them. Similar to these weight experts there are numerous specialists who give instructions in the manufacture of certain specialties, such as the production of old and new kinds of varnished, colored or ornamental leathers. From the large number of experts in various lines, it can be seen that it is very difficult to make sure that one is selecting the right man for special work. For this reason the above-mentioned information bureau could be made of inestimable value and through it, no doubt, many questions of great importance to the leather industry would be introduced. L. A. C.

Caesalpinia digyna as a Tanning Material. *Bull. Imp. Inst.*, through *Leather World*. The pods of Caesalpinia digyna are called Teri and come from Burma. Other species of Caesalpinia furnish the well-known algarobilla and divi-divi. Good specimens of teri contain from 45 to 60 per cent. tannin (dry basis). The present supply is very small. In order to render this excellent material available, it would have to be cultivated on a large scale.

Tannin from Chinese Gall Nuts. K. FEIST AND HEINRICH HAUN. *Chem.-Ztg.*, 1912 [36], 1201-2. Most authorities regard tannin as digallic acid and attribute the occasional glucose content to impurity. No distinction has been made so far between the tannin from Turkish and Chinese gall nuts but since 1880 the latter source has contributed to the market. One of the authors (Feist) examined Turkish gall nuts in 1908 (abstr. this JOURNAL, 1909 (IV) 63) and found in these and the tannins prepared therefrom, a crystalline substance, glucogallic acid which could be split into one molecule each of glucose and gallic acid. After freeing the tanning from glucogallic acid it still yielded glucose. Chinese gall nuts subjected to a similar extraction gave gallic acid but no glucotannic acid. The tannin was then prepared in the same way as that from Turkish galls and subjects to hydrolysis by boiling with dilute H_2SO_4. The product was extracted with ether and the ether-freed residue again boiled and re-extracted and so on. After 14 such operations the ether extract yielded 93.5 per cent. gallic acid (tannin = 100) and the aqueous residue after treatment with basic lead acetate yielded 5.6 per cent. glucose. Strict quantitative results cannot be expected since a small amount escapes hydrolysis and is ppt. by the lead solution, some carbonization results and finally glucose is partly destroyed during the protracted boiling. The authors have found the loss of glucose during hydrolysis of tannin to be over 20 per cent. in some experiments. The optical rotation measurements are cited in detail for various preparations from the two varieties of gall nuts but the results were found variable and irregular and no conclusions are drawn. Investigations are in progress upon the methylation products of the two tannins as well as of glucotannic acid. W. J. K.

Digitized by Google

Dyeing Calf Skins. *Ledertechn. Rundschau.*, 1912, 289-90. Like silk among textiles, calf is easiest dyed among the leathers. It is important to carefully prepare the skins before dyeing. They are first softened in lukewarm water, then stamped for one hour in a wooden vessel with a wooden beetle, next agitated with water of 40° C., drained, stamped another hour and rinsed. When finished, they should feel slimy to the touch. On a larger scale the drum is used.

Before dyeing, the skins are spread in pairs (made up of equal sizes) flesh to flesh upon a zinc or glass table in order to smooth the folds and save dye by protecting the flesh. For light brilliant colors, potass. chromate is the best mordant, 10-20 grms. to each skin. Alum is also used and is generally not very satisfactory. After agitation in the mordant bath for 10 min., the skins go into the second bath containing a portion of the dye and are finally dipped into the third bath of full strength dye. Acetate of iron is used as the mordant for middle colors and nitrate or sulphate for dark tones. Lime in the water is injurious and should first be neutralized with acetic acid. The iron solution should be diluted to 10° B. since the concentrated solution of commerce 30° B.) would darken the hue too rapidly and unevenly. Rinsing in cold water should not follow the iron bath, or the skins become hard.

These directions are only for basic dyes and not suited for acid colors. In mixing dyes, only those of the same class should be combined, although a basic dye in a separate bath may follow an acid dye.

W. J. K.

Vache Leather Tannage (by a "tanner"). *Ledertechn. Runaschau.*, 1912, 313-7. Although this manufacture seems simple, it demands full technical skill and the product must satisfy a mass of requirements. The first foundation is a good watering; failing, the leather is spotted and dead. Salt hides require 2-3 days; 6 hours in the first water, then 12, 12 and 12-24 hours, draining well at each transfer, best on inclined horses. Dried hides require longer soaking. Old water is often preferred and may be used according to the season if not too foul. Fresh river water is, however, better. The drum has its advantages and with proper judgment, alkali can be sometimes used.

Good rendement and retention of hide substance depend upon rapidity in liming as well as soaking; fresh lime, sharpened with sod. sulphide, permits this. It is best to begin with a used lime from the preceding lot and transfer thence to a fresh sharpened lime which is bettered the second day; the liming is complete in 4-5 days. The hides are unhaired in warm water and then left for 2 days in a weak bath of pure lime in order to swell for tannage. The deliming with lactic acid is carried out fastest in the drum. A temperature of 22° C. should not be exceeded in liming.

Digitized by Google

The preparation for pit tannage is in the handler vats and here the constant renewal and revival of the liquors is essential and the formation of acid and the consequent decomposition of tannin must be avoided as much as possible. The so-called tanning acid, a secondary product from the carbohydrates accompanying the tannins, no wise promotes tannage or a healthy permanent swelling. The hide has previously been sufficiently swelled and only needs filling directly with tannin. The liquors used for pit tannage should contain but moderate amounts of sugar-containing tan stuffs, like myrabolans and be so adjusted that the real tanning substances preponderate. A used liquor drawn from the "Versenks" or lay-aways as well as from the corresponding spent barks should not be used again in the vats or pits before being refreshed and filtered through new bark in suitable extractors or leaches. This removes the injurious bacteria as well as strengthens the liquor. Returning to the handlers, it is not sufficient to forward the hides progressively through weak to strong liquors, but each vat should receive a daily addition of fresh liquor, the process beginning with 1° B. and ending after about 8 days with 3-4° B. in the last vat. The addition of extra acid to the vats is an error; a corresponding amount of useful, diffusible tannin is destroyed and that remaining is precipitated around the fibers, producing brittle leather. Falling down of the hide in the vats is decidedly to be avoided and cannot happen if the rules given are followed.

From the vats the hides go to the "Versenks" in liquors of 3½ to 4° B.; dusting mixtures, 5 parts quebracho and pine, 4 parts oak and myrabolans. The time for the first "Versenk" is about 3 weeks, for the second 4 weeks. For this, a liquor of 4-4½° B. is used and a greater proposition of quebracho and oak. The tannage is finished in a lay-away with oak and a little valonea. Often the tanning is completed with special extracts in the drum.

This leads to the discussion of drum tannage proper; a rapid process, furthered by the use of strong liquors, high temperature and agitation. The hide fiber does not suffer in this accelerated process if the established rules be adhered to. The liquor required for complete tannage is not placed in the drum at once but in at least three portions. The reaction is started with a small amount, reaching 47-8° C. after a few hours rotation, but this temperature should not be exceeded; overheating makes the leather brittle. The tannage begins with liquor of 6-7° B. and finishes after 3 days at the most, with 9-10° B. When the specified temperature is reached the drum is stopped, opened and let cool, the tannage continuing meanwhile. The drum should be only slightly over half full. Sulphites or acids ought not be added to the liquor; small amounts of tanning oil may be used.

After tannage the hides lie in piles covered with moist cloths for 2-3 days, that the tannin may become fixed. In preparing for currying the drum-tanned leather is watered a few hours in a weak liquor, then 2-3 hours in pure water. Pit-tanned leather is simply rinsed. Either

Digitized by Google

leather is then oiled on the grain and let dry to the extent desired for currying. W. J. K.

PATENTS.

Oil Tannage. British Patent No. 13,126. J. LEWKOWITSCH and J. T. WOOD. Fatty acids derived by saponification from animal oils are used for making chamois leather and preparing degras, moëllon, sod oil, etc., therefrom. The fatty acids are prepared by any well-known method of saponification, as used in the candle-making or soap-making industries, and are used as a stocking medium in place of the usual commercial oils, the skins being subsequently pressed and washed for the recovery of the fatty material for making degras, etc.

Leather-splitting Machine. U. S. Patents Nos. 1,038,560 and 1,038,561. JOSEPH H. GAY, Newark, N. J.

Process of Tanning. U. S. Patent No. 1,039,150. GUSTAF HJALMER LINDSTROM, New Plymouth, New Zealand. After being unhaired and cleaned, the hides are treated with a solution of alum, salt, and pyrophosphate of soda, and then with a mixture of such solution and gambier and quebracho, with borax baths alternating with the tanning liquors.

Production of Leather. U. S. Patent No. 1,040,400. E. E. M. PAYNE, Aylesbury, England. The process consists in treating the hides with an alkaline peat extract and afterward with an acid.

Artificial Leather. British Patent No. 12,991. J. F. LIPMAN, London. Leather waste is treated with carbon bisulphide, potash permanganate and lime, heated to 212° F. with stirring, moulded, dried and rolled.

Artificial Leather. British Patent No. 15,761. E. REIDEL, Mannheim, Germany. A sheet material for belting, or for boot soles, etc., is made from dried slaughter-house residues, such as tendons, sinews, or entrails, by reducing them to long thin filaments which are combined crosswise into a mat, immersed in a swelling-bath, washed, treated with albumen, pressed, tanned, and dried. Hemp, flax, tow, manila, aloe, sisal, or other long vegetable filaments may be added to the animal matter. The swelling-bath may contain a dilute alkali, such as sodium sulphide, or an acid, such as sulphuric, hydrochloric, lactic, or propionic acid, and the albumen may be in the form of blood, globulin, or fibrin. A saturated soap solution or an amulsion or ceresin or paraffin may be used with the albumen; or it may be used after the tanning and then be fixed by means of metallic salts. In an alternative treatment, the swelling-bath is omitted, the matted substance being treated directly with albumen and soap solution, pressed, and tanned.

Digitized by Google

Digitized by Google

Digitized by Google

342814 TS940 A6 v.7 FORESTRY
American leather chemists association Journal
Catalog Dept.
(Trustees)
TS940 342814
A6
v.7
Forestry
amer.
UNIVERSITY OF CALIFORNIA LIBRARY
Digitized by Google

Digitized by Google

342814 TS940 A6 v.7 FORESTRY
American leather chemists association Journal
Catalog Dept.
(Forestry)
TS940 342814
A6
v.7
Forestry
amer.
UNIVERSITY OF CALIFORNIA LIBRARY
Digitized by Google

Digitized by Google

American leather chemists association Journal

A6
v.7
FORESTRY

Catalog Dept.
(Forestry)

TS940
A6
v.7
Forestry
amer.

342814

UNIVERSITY OF CALIFORNIA LIBRARY

Digitized by Google

Digitized by Google